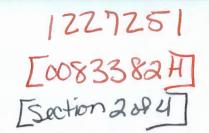


DOE/RL-2010-95, REV. 0



# 4 Nature and Extent of Contamination

Evaluation of the nature and extent of contamination describes contaminant concentrations found in the environmental media in the study area. Contamination is determined from recently collected RI and RPO data, data from the Columbia River RI Work Plan (DOE/RL-2008-11), data from the RCBRA (DOE/RL-2007-21, Volume I), data available from previous LFIs, ongoing air and water monitoring, completed interim remediation (that is, CVP data), and historical operational process information. Reported concentrations of the various analytes are compared to vadose zone background concentrations as an initial screening tool to identify contaminants of potential concern (COPCs) associated with 19 sites within 100-D/H.

Following the comparison to background levels, the contaminants are described in relation to their nature and extent. As such, this chapter focuses principally on vadose zone and groundwater COPCs. Uncertainties associated with the data, as they relate to the nature and extent of contamination, also are described. These contaminants (also referred to as COPCs) are evaluated in Chapters 5, 6, and 7 to determine if their concentrations exceed soil screening levels or preliminary remediation goals developed for the protection of groundwater, surface water, human health and ecological receptors. Contaminants that are determined to exceed these PRGs warrant further evaluation in the feasibility study and are referred to as a contaminant of concern (COC).

# Highlights

- Analytes detected in the vadose zone were compared to background concentrations. Initial screening identified more than 70 analytes above background concentrations (see Table 4-6).
- COPC concentrations in the vadose zone vary with depth. However, most contaminant concentrations generally decrease with depth. Higher concentrations are typically in the upper half of the vadose zone.
- Cr(VI) plumes in groundwater are associated with past reactor operations at 100-D and 100-H.
   Migration from 100-D across the Horn toward 100-H has resulted in a large connected Cr(VI) plume within D/H with an area greater than 10 km² (3.86 mi²).
- Cr(VI) contamination has been identified in the first water-bearing unit within the RUM at 100-H near the river, and in one well in the Horn.
- Nitrate plumes are present primarily in 100-D coincident with the Cr(VI) plume with elevated nitrate at selected wells in 100-H.
- Strontium-90 is present in a small plume in 100-H east of the reactor and in one well in 100-D. These localized areas are associated with the fuel storage basins.
- Several likely continuing sources of Cr(VI) to groundwater contamination are identified at waste sites (for example, 100-D-100, 100-D-104, and 100-D-30) undergoing active remediation.

Chapter 4 of the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) described the major features of the CSM. These concepts provide the basic framework for interpreting the data collected under the RI to fulfill the data gaps and data needs developed in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). Section 4.7 of this RI report presents refinement and discussion of the CSM in the context of the results. This chapter continues to develop the CSM with nature and extent information regarding 100-D/H media (soil, groundwater, air, biota, and surface water/sediment).

Contaminants in the vadose zone, periodically rewetted zone (PRZ), and groundwater resulted from various activities during reactor operations. Under current conditions, the primary contributor to groundwater contamination at 100-D/H is vadose zone contamination from unremediated waste sites (for example, Cr(VI) from 100-D-100, 100-D-30, and 100-D-104). Contaminants from waste sites and facilities were transported through the vadose zone, into the PRZ, and then into the groundwater. Less mobile contaminants tend to stay bound to soil particles in the vadose zone and PRZ, while more mobile contaminants tend to move through the vadose zone and PRZ into the groundwater, due to infiltration and changing groundwater elevations caused by Columbia River stage changes.

Much of the data collected during implementation of interim remedial actions has been documented in CVPs and LFIs, which are incorporated into the discussion of the nature and extent of contamination.

100-DR-1,2 100-HR-1,234-1

Information is also presented to describe the current understanding of contamination attributed to 100-D/H in the Columbia River, biota, and air, and is summarized from the Hanford Site Releases Data Summary (WCH-398), RCBRA (DOE/RL-2007-21, Volume I), and *Hanford Site Environmental Report for Calendar Year 2011* (DOE/RL-2011-119). Section 4.3 describes vadose zone contamination associated with locations selected for new boreholes/wells under the Rl. Section 4.4 describes groundwater contamination. Sections 4.4.5, 4.5, and 4.6 discuss Columbia River surface water/sediments, biota, and air, respectively.

# 4.1 Background Concentrations

Background substances are usually naturally occurring (present in the environment in forms not influenced by human activity) or anthropogenic (natural and/or artificial forms present in the environment due to human activities not related to the CERCLA site(s) under consideration). Some chemicals may be present in background because of both natural and artificial conditions, such as naturally occurring arsenic and arsenic from historical agricultural pesticide applications (*Guidance for Comparing Background and Chemical Concentrations in Soil for CERCLA Sites* [EPA 540-R-01-003]).

The identification of background concentrations of substances in soil is one step in determining if potential waste sites require remedial action. These concentrations are also important because in some instances, calculated risk-based benchmarks (substance concentrations that may have the potential to present risk to human or ecological receptors) are less than background levels. Where benchmarks are less than background levels, cleanup goals generally default to background (rather than the calculated values) because CERCLA typically does not require cleanup to concentrations below background levels.

The background concentrations used in this section represent 90<sup>th</sup> percentile values that are determined from a range of Hanford Site background sample concentrations. For example, the 104 total chromium background sample concentrations used to calculate the 90<sup>th</sup> percentile soil value (18.5 mg/kg) ranged from 2.9 to 30.6 mg/kg. Similarly, the 104 lead background sample concentrations used to calculate the 90<sup>th</sup> percentile soil value (10.2 mg/kg) ranged from 1.1 to 26.6 mg/kg. As such, contaminant concentrations may exceed the 90<sup>th</sup> percentile background value and remain within the range of natural Hanford Site background. As part of the RI, supplemental investigations developed River Corridor background soil values for antimony, boron, cadmium, lithium, mercury, molybdenum, selenium, silver, and thallium. The investigation results are in *Soil Background Data for Interim Use at the Hanford Site* (ECF-HANFORD-11-0038), with sample results found in Appendix D (Table D-69).

In addition to background concentrations of metals, orchard lands are potential contributors of arsenic and lead to the soil. Collocated within the historical orchard land areas are waste sites related to releases from Hanford Site operations (Figure 4-1). The 100-OL-1 OU has been established in the 100 Area and sections of 100-DH to address residual lead and arsenic contamination in the soil from pre-Hanford agricultural pesticide use. The contaminants associated with these waste sites will continue to be evaluated and addressed through the RI/FS process for the various areas (100-BC, 100-K, 100-N, 100-D/H, or 100-F/IU) where the individual waste sites are geographically located. During implementation of the selected remedy at these waste sites, contaminants present will be remediated as needed to meet the cleanup levels prescribed in the applicable ROD. Should contaminants associated with historical orchard lands (for example, lead, and arsenic) be present at any particular waste site, that contamination will not be remediated beyond the waste site footprint as part of the ROD. Any contaminants remaining outside the waste site footprint will be addressed as part of the remedial investigation for the 100-OL-1 OU. This approach will allow reclassification of individual waste sites that meet the cleanup standards (for non-orchard lands related contaminants) of the applicable decision area ROD while supporting the broad area investigation of historical orchard lands as part of the 100-OL-1 OU.

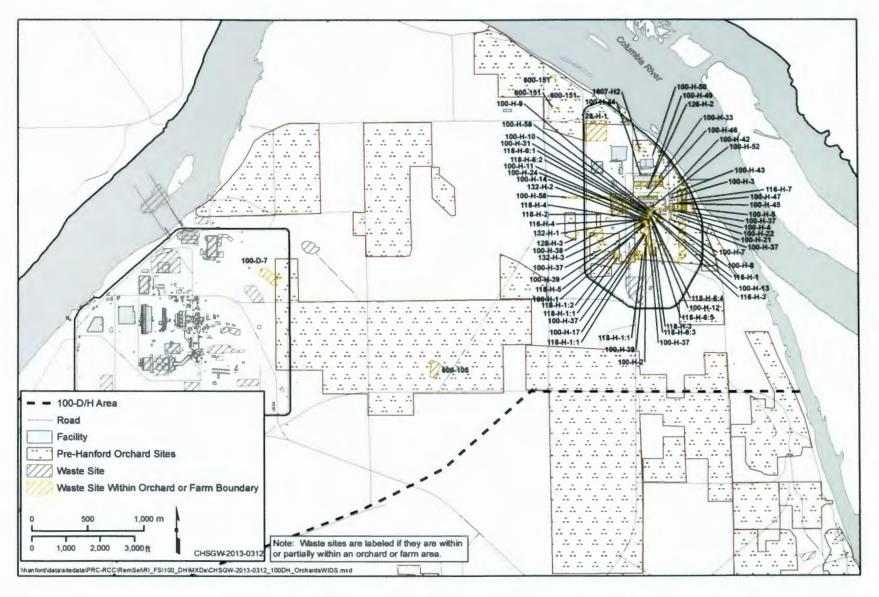


Figure 4-1. Locations of Former Orchards and Waste Sites in 100-D/H

Details for the handoff of actions between the decision area RODs and the 100-OL-1 OU investigations will be established in the remedial design report/remedial action work plan (RDR/RAWP) documents associated with each decision area ROD. An example of this approach as implemented for the interim action RODs is provided by Federal Facility Agreement and Consent Order, Modify Remedial Design Report/Remedial Action Work Plan for the 100 Area (DOE/RL-96-17, Rev. 6) to Add Section 3.6.10 Residual Pesticides from Agriculture Use (TPA-CN-401).

Soil background values are benchmarks to define contamination, as well as identify preliminary COPCs. Soil analytes that do not have established background concentrations, but are detected at concentrations greater than method detection limits are also considered preliminary COPCs and are further evaluated in Chapters 5, 6, and 7. The groundwater background values are primarily reference points and are not applied to the discussion of groundwater contamination. This is because filtered samples were used to develop groundwater background values due to the variability of geochemical conditions across 100-D/H. Tables 4-1 and 4-2 present background soil and groundwater concentrations, respectively, derived for the Hanford Site.

Table 4-1. Background Concentrations in Hanford Site Soil

Radionuclides (pCi/g)					
Analyte	CAS Number	Abbreviation	Half-life (yrs)	90 <sup>th</sup> Percentile	Reference
Americium-241	14596-10-2	Am-241	458		
Carbon-14	14762-75-5	C-14	5,730		
Cesium-137 <sup>a</sup>	10045-97-3	Cs-137	30	1.05	DOE/RL-96-12
Cobalt-60	10198-40-0	Co-60	5.3	0.00842	DOE/RL-96-12
Europium-152	14683-23-9	Eu-152	12.7		
Europium-154	15585-10-1	Eu-154	16	0.0334	DOE/RL-96-12
Europium-155	14391-16-3	Eu-155	1.8	0.0539	DOE/RL-96-12
Neptunium-237	13994-20-2	Np-237	2.1 million		***
Nickel-63	13981-37-8	Ni-63	92		
Plutonium-238	13981-16-3	Pu-238	86.4	0.00378	DOE/RL-96-12
Plutonium-239/240 <sup>a</sup>	15117-48-3	Pu-239/240	24,000	0.0248	DOE/RL-96-12
Strontium-90 <sup>a</sup>	10098-97-2	Sr-90	29.1	0.178	DOE/RL-96-12
Technetium-99	14133-76-7	Tc-99	211,000		
Tritium	10028-17-8	H-3	12.3		
Uranium-233/234	13966-29-5	U-233/234	160,000	1.10	DOE/RL-96-12
Uranium-235	15117-96-1	U-235	710 million	0.109	DOE/RL-96-12
Uranium-238	7440-61-1	U-238	4.5 billion	1.06	DOE/RL-96-12

Table 4-1. Background Concentrations in Hanford Site Soil

Nonradionuclides (mg/kg)				
Analyte	CAS Number	Abbreviation	90 <sup>th</sup> Percentile	Reference
Aluminum	7429-90-5	Al	11,800	DOE/RL-92-24
Antimony	7440-36-0	Sb	0.13	ECF-HANFORD-11- 0038
Arsenic	7440-38-2	As	6.47	DOE/RL-92-24
Barium	7440-39-3	Ba	132	DOE/RL-92-24
Beryllium	7440-41-7	Be	1.51	DOE/RL-92-24
Boron	7440-42-8	В	3.89	ECF-HANFORD-11- 0038
Cadmium	7440-43-9	Cd	0.56	ECF-HANFORD-11- 0038
Chromium (total) (filtered)	7440-47-3	Cr	18.5	DOE/RL-92-24
Chromium (Hexavalent)	18540-29-9	Cr(VI)		
Cobalt	7440-48-4	Со	15.7	DOE/RL-92-24
Copper	7440-50-8	Cu	22.0	DOE/RL-92-24
Lead	7439-92-1	Pb	10.2	DOE/RL-92-24
Lithium	7439-93-2	Li	13.3	ECF-HANFORD-11- 0038
Manganese	7439-96-5	Mn	512	DOE/RL-92-24
Mercury	7439-97-6	Hg	0.01	ECF-HANFORD-11- 0038
Molybdenum	7439-98-7	Мо	0.47	ECF-HANFORD-11- 0038
Nickel	7440-02-0	Ni	19.1	DOE/RL-92-24
Selenium	7782-49-2	Se	0.78	ECF-HANFORD-11- 0038
Silver	7440-22-4	Ag	0.167	ECF-HANFORD-11- 0038
Strontium metal (strontium)	7440-24-6	Sr		to to
Thallium	7440-28-0	TI	0.18	ECF-HANFORD-11- 0038
Vanadium	7440-62-2	V	85.1	DOE/RL-92-24
Zinc	7440-66-6	Zn	67.8	DOE/RL-92-24
Fluoride	16984-48-8	F	2.81	DOE/RL-92-24
Nitrate	14797-55-8	NO <sub>3</sub>	52	DOE/RL-92-24
Nitrite	14797-65-0	NO <sub>2</sub>	b	DOE/RL-92-24

Table 4-1. Background Concentrations in Hanford Site Soil

	Nonradionuclides (mg/kg)				
Analyte	CAS Number	Abbreviation	90 <sup>th</sup> Percentile	Reference	
1,1-Dichloroethene	75-35-4				
1,4-Dichlorobenzene	106-46-7				
Acenaphthene	83-32-9				
Anthracene	120-12-7				
Aroclor-1016	12674-11-2				
Aroclor-1221	11104-28-2				
Aroclor-1232	11141-16-5				
Aroclor-1242	53469-21-9				
Aroclor-1248	12672-29-6				
Aroclor-1254	11097-69-1			N 20-	
Aroclor-1260	11096-82-5				
Benzene	71-43-2				
Benzo(a)anthracene	56-55-3			- th	
Benzo(a)pyrene	50-32-8				
Benzo(b)fluoranthene	205-99-2				
Benzo(k)fluoranthene	207-08-9		-10 GD		
Benzo(ghi)perylene	191-24-2				
Bis(2-ethylhexyl)phthalate	117-81-7			nior fields	
Carbazole	86-74-8				
Carbon tetrachloride	56-23-5	CCl <sub>4</sub>			
Chloroform	67-66-3	CHCl <sub>3</sub>			
Chrysene	218-01-9				
Dibenz[a,h]anthracene	53-70-3				
Di-n-butylphthalate	84-74-2				
Ethylene Glycol	107-21-1				
Fluoranthene	206-44-0				
Indeno(1,2,3-cd)pyrene	193-39-5			direk	
Methylene Chloride	75-09-2	CH <sub>2</sub> Cl <sub>2</sub>			
Pentachlorophenol	87-86-5				
Phenanthrene	85-01-8				
Pyrene	129-00-0			W-00	

Table 4-1. Background Concentrations in Hanford Site Soil

Nonradionuclides (mg/kg)					
Analyte	CAS Number	Abbreviation	90 <sup>th</sup> Percentile	Reference	
Tetrachloroethene	127-18-4	PCE			
Trichloroethylene	79-01-6	TCE		m.m	
Toluene	108-88-3				
Total Petroleum Hydrocarbons	68334-30-5	ТРН			

Sources: Hanford Site Background: Part 1, Soil Background for Nonradioactive Analytes (DOE/RL-92-24).

 $Hanford\ Site\ Background:\ Part\ 2,\ Soil\ Background\ for\ Radionuclides\ (DOE/RL-96-12).$ 

Soil Background Data for Interim Use at the Hanford Site (ECF-HANFORD-11-0038).

- a. Cesium-137, strontium-90, and plutonium-239/240 are anthropogenic radionuclides whose background values only apply to surface soil samples.
- b. Insufficient data above the reporting limit to provide for a distribution fit.
- -- = either a background study has not been performed for this analyte (i.e., strontium) or the constituent does not occur naturally in the environment (i.e., the organic constituents).

Table 4-2. Hanford Site Groundwater Background Concentrations for COPCs in 100-D/H Groundwater

Constituent	Units	90 <sup>th</sup> Percentile			
Nonradionuclides					
Antimony (filtered)	μg/L	55.1			
Arsenic (filtered)	μg/L	7.85			
Barium (filtered)	μg/L	105			
Beryllium (filtered)	μg/L	2.29			
Cadmium (filtered)	μg/L	0.916			
Chloride (unfiltered)	μg/L	15,630			
Chromium (total) (filtered)	μg/L	2.4			
Cobalt (filtered)	μg/L	0.916			
Copper (filtered)	μg/L	0.81			
Cyanide	μg/L	8.41			
Fluoride	μg/L	1,047			
Lead (filtered)	μg/L	0.917			
Manganese (filtered)	μg/L	38.5			
Mercury (filtered)	μg/L	0.003			
Nickel (filtered)	μg/L	1.56			

Table 4-2. Hanford Site Groundwater Background Concentrations for COPCs in 100-D/H Groundwater

Constituent	Units	90th Percentile
Nitrate (unfiltered)	μg/L	26,871
Nitrite (unfiltered)	μg/L	93.7
Selenium (filtered)	μg/L	10.5
Sulfate (unfiltered)	μg/L	47,014
Thallium (filtered)	μg/L	1.67
Uranium	μg/L	9.85
Vanadium (filtered)	μg/L	11.5
Zinc (filtered)	μg/L	21.8
	Radionuclides	
Strontium-90	pCi/L	0.0146
Tritium	pCi/L	119

Source: Hanford Site Background: Part 3, Groundwater Background (DOE/RL-96-61).

Note: The organic COPCs 1,1-dichloroethene, 1,1,2-trichloroethane, benzene, carbon tetrachloride, chloroform, tetrachloroethene, TCE, and vinyl chloride are assumed to have natural background concentrations of zero.

COPC = contaminant of potential concern

Filtered and unfiltered samples were used to develop Table 4-2, as described in detail in Chapter 6 of *Hanford Site Background: Part 3, Groundwater Background* (DOE/RL-96-61). Use of filtered or unfiltered samples was evaluated based on the sample size and distribution. All samples were evaluated on a statistical basis, and where values were similar, the filtered status was not specified.

## 4.2 Sources

Section 1.2.2 discusses the site history of 100-D/H. The primary sources of contamination in 100-D/H are liquid and solid wastes generated and released during the operation of the reactors and support facilities, and from unplanned releases. The reactor operations responsible for generating and releasing contaminants to the environment have all been discontinued. Secondary sources are contaminants remaining in the vadose zone and within the aquifer matrix. This section discusses what is considered a primary source and what is considered a secondary source (Figure 4-2), and highlights certain COPCs because of their observed distribution or persistence in the environment at 100-D/H. The same individual contaminants may be found in both the original primary source material that was released (for example, liquid and solid waste streams discharged to the environment), and in the secondary sources that remain (for example, contaminated vadose zone soil). Contaminants that are currently present in secondary sources were typically released as primary source material. Limited primary source material may be encountered during the implementation of remedial activities in structures, pipelines, and other process components. Residual material remaining in piping is typically found as pipe scaling and has a limited potential to be released as a secondary source to the vadose zone. Assessment of the potential for continuing releases from remaining secondary sources is an element of the remedial investigation.

Figure 4-2. Graphical Example of Primary and Secondary Sources

Liquid waste sources can be classified into two types: high volume/low concentration liquid wastes and low volume/high concentration liquid wastes. The volumes of liquid effluent waste streams varied over orders of magnitude. The largest volume streams were generated as steam condensate, cooling water, and unplanned releases. To generate the cooling water solutions for the 105-D, 105-DR, and 105-H Reactors, concentrated sodium dichromate solid and liquid feed solutions were mixed in the cooling water system to achieve the required coolant concentration. As discussed in Chapter 1, the primary contaminants related to the cooling water include Cr(VI), tritium, strontium-90, and various radionuclides, with the radionuclides being a result of the cooling water passing through the reactors.

Solid wastes in 100-D/H were generated in facilities and managed mainly in burial grounds. According to WIDS, the burial grounds consist of numerous trenches of various sizes that contain radioactive solid waste from the 105-D, 105-DR, and 105-H Reactors. Solid wastes were also disposed into burn pits and dumping areas, and as unplanned releases. Section 1.2.2.2 describes the various types of waste disposal areas, such as trenches.

# 4.2.1 Primary Sources

The primary sources of contamination in 100-D/H are three water-cooled nuclear reactors (105-D, 105-DR, and 105-H [Figure1-2]), and the structures (for example, fuel storage basins) and processes (for example, sodium dichromate process) associated with reactor operations. The three reactor buildings remain intact today in a safe storage enclosure. Most of the associated structures and facilities near the reactor have been demolished or removed. The reactors were built to irradiate uranium-enriched fuel rods from which plutonium and other special nuclear materials could be extracted. The reactors and processes associated with operations generated large quantities of liquid and solid wastes. Effluent generated during operations consisted primarily of contaminated reactor cooling water, fuel storage basin water, and decontamination solutions. Cooling water consisted of river water treated to remove dissolved solids and enhanced with chemicals to reduce corrosion. Cooling water contaminants consisted of fuel materials, fission and irradiation byproducts, and Cr(VI) (used as a corrosion inhibitor). Solid wastes consisted of sludge, reactor components, and various other contaminated items. Waste generated from reactor operations was contaminated with radionuclides, hazardous chemicals, or both.

The target analyte list for contaminants in soil was based on process knowledge, as described in the 100-D/H SAP (DOE/RL-2009-40)). COPCs in groundwater were developed for the 100-D/H SAP (DOE/RL-2009-40) as described in *Identification of Contaminants of Potential Concern for Groundwater Risk Assessment at the 100-HR-3 Groundwater Operable Unit* (ECF-100HR3-10-0469). Tables 2-3 through 2-18 of the 100-D/H SAP (DOE/RL-2009-40) present the waste site-specific target analytes and analytical methods for determination of the analytes.

**Liquid Effluent Waste Sources.** The volumes of liquid effluent waste streams discharged to specific waste sites varied over several orders of magnitude. The largest volume streams were generated as steam condensate, cooling water, and unplanned releases of cooling water. The primary contaminants related to the cooling water include Cr(VI), carbon-14, tritium, strontium-90, and various other radionuclides.

Concentrated Water Treatment Chemical Waste Sources. Substantial volumes of chemicals were used to condition the cooling water used by the reactors. These include chlorine, sulfuric acid, alum, sodium chloride, sodium hydroxide, and sodium dichromate dihydrate. These chemicals were stored in bulk at the water treatment head houses for each reactor (183-D and 183-H) and were metered into the cooling water stream at various points ultimately to provide a continuous

stream of cooling water with low solids and conditioned for corrosion resistance. Over the course of operations, varying volumes of these chemicals were released to the environment, either routinely or episodically, in the vicinity of the chemical storage and handling areas. The sources consisted of low-volume, high-concentration sodium dichromate and variable volumes of low-concentration sodium dichromate in liquid effluent. To generate the cooling water solutions for the 105-D, 105-DR, and 105-H Reactors, concentrated sodium dichromate feed solutions were processed through an infrastructure system that diluted the higher-strength source materials to achieve the required coolant composition. Reactor operations at 100-D/H used both concentrated sodium dichromate solution and granular sodium dichromate (see Figures 1-14 and 1-15).

Solid Waste Primary Sources. The primary solid waste source area types are buildings, burial sites, and solid waste sites. The 118-D-3 and 118-D-4 Burial Grounds were the primary disposal sites for radioactive solid wastes at 100-D. The primary disposal site for radioactive solid waste from the 105-H Reactor was the 118-H-1 Burial Ground. However, numerous other burial grounds received radioactive waste at 100-D/H. Solid wastes disposed to these waste sites include a variety of radiologically contaminated and irradiated materials consisting of reactor hardware including irradiated dummy fuel elements, splines, rods, thimbles, and various other solid, and potentially liquid, waste in containers. These waste sites consist of numerous trenches and vertical steel pipes of various sizes that contain radioactive solid waste from 105-D, 105-DR, and 105-H Reactors. Waste from the 105-N Reactor was also disposed at 100-D. Occasional fires at burial grounds were the source of unplanned releases.

**Coal Ash Sites.** Coal-fired power plants were associated with the D and H reactors. Coal ash is considered a solid waste issue at 100-D/H. There are two coal ash waste sites in 100-D/H, including two sites that are classified as "rejected" waste sites—126-D-1 and 126-H-1. Coal ash sites are not considered to constitute hazardous wastes; therefore, these sites are not considered further under CERCLA. If debris is removed from these sites in the 100-D/H area, it will be disposed of in approved solid waste disposal facilities.

Nonoperational Areas and Orphan Sites. The nonoperational areas at 100-D/H have been evaluated through the OSE process described in Appendix K. This evaluation includes not only the potential for anthropogenic disposal activities but also considers windblown dust emissions, stack emissions, overland flow, and possible contaminant placement because of biointrusion by potential carriers such as wasps. An historical evaluation was performed inside the exclusion area and walk-downs conducted outside the exclusion area. New discoveries of waste sites not associated with existing waste sites is unlikely.

Secondary Sources. Contaminants released to the environment during reactor operations contaminated the vadose zone beneath facilities and waste sites. These secondary sources of contamination pose potential human health and the environment exposures through numerous pathways (for example, direct contact, inhalation, and/or ingestion of contaminated soil, groundwater, and/or surface water). Contaminants from waste sites and facilities were transported through the vadose zone, into the periodically rewetted zone (PRZ), and then into the groundwater. Less mobile contaminants tend to stay bound to soil particles in the vadose zone and PRZ, while more mobile contaminants tend to move through the vadose zone and PRZ into the groundwater due to driving forces (during reactor operations and under natural rainfall conditions). As groundwater elevations rise and fall across the PRZ due to Columbia River stage changes, contaminants that are more mobile have the potential to leach into the groundwater. This includes contaminated soil in the PRZ, which is the lower portion of the vadose zone that is contacted by groundwater during periods of high groundwater elevation.

Chapter 1 presents the operational periods of the facilities and reactors. The reactor processes responsible for generating and releasing primary sources to the environment have all been discontinued. Contaminants remaining as secondary sources may continue to migrate through the environment, depending on environmental conditions, and the individual constituent properties. Section 4.2.3 lists the constituents detected in 100-D/H groundwater samples collected since 2005.

Chapters 6 and 7, respectively, discuss the evaluation of risks posed by the identified secondary sources to human health and the environment through direct exposure. Interim actions continue to address the risks posed by contaminants.. The potential for secondary sources to provide a significant ongoing source of contamination to groundwater is evaluated through the comparison of post remedial action contaminant concentrations to the screening levels for groundwater and surface water protection in Chapter 5.

The following sections briefly discuss contaminants seen in the vadose zone and in groundwater. Contaminants present in the vadose zone have the potential to affect human health and the environment through direct exposure, and are identified in Chapter 8, Tables 8-2 and 8-3. Four of these contaminants are shown to have affected groundwater at 100-D/H—Cr(VI), total chromium, nitrate, and Sr-90. The RI results and pertinent historical data for the vadose zone and groundwater are presented in more detail in Sections 4.3 and 4.4, respectively.

# 4.2.2 Sources of Specific Contaminants at 100-D/H

The major contaminants of interest at 100-D/H originated from chemical materials used during reactor operations. The following paragraphs discuss the processes that contributed these contaminants to the environment.

## 4.2.2.1 Hexavalent Chromium

In the hexavalent state (Cr(VI)), chromium is present as a soluble oxyanion and because of its mobility and widespread presence, has a potential effect on human health and the environment (100-HR-3 and 100-KR-4 Interim ROD [EPA/ROD/R10-96/134]; 100-D/H Work Plan [DOE/RL-2008-46-ADD1]). Cr(VI) is present in the groundwater at 100-D/H at concentrations exceeding aquatic ("Toxics Criteria for Those States Not Complying with Clean Water Act Section 303(c)(2)(B)" [40 CFR 131.36]) and 2007 MTCA (WAC 173-340) B levels.

During operation of the D, DR, and H Reactors and associated facilities, numerous locations received highly concentrated sodium dichromate solutions. This stock solution was fed into the cooling water treatment system for mixing and dilution before entering the reactors. After passing through each reactor, the low-concentration sodium dichromate solutions were discharged to retention basins and selected trenches and cribs. After operations, reactor decontamination wastes were discharged to the 116-DR-1&2 Trench. Figures 1-15 and 1-16 show facilities where sodium dichromate was handled.

Sodium dichromate dihydrate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-2H<sub>2</sub>O), the chemical form of the treatment product containing Cr(VI), was delivered as a solid and concentrated 70 wt % liquid by rail tanker cars and was transferred to aboveground bulk storage tanks. It was added to the reactor cooling water to inhibit corrosion (*100-D Area Technical Baseline Report* [WHC-SD-EN-TI-181]). Figure 1-12 shows the general flow path of the sodium dichromate. Solid sodium dichromate was stored and mixed with water at the 108-D Building Chemical Pump House and the 185-D Deaerating Plant from 1955 until 1959. The concentrated solution, containing about 700 g/L sodium dichromate

dihydrate, was metered into the cooling water feed stream to achieve a working concentration of to  $2,000 \mu g/L$ . By 1964, that amount was reduced to  $1,000 \mu g/L$  (see Section 1.2.2.5.).

The quantities of sodium dichromate received, handled, and processed each month in 100-D/H were essentially the amount needed to provide the  $2,000~\mu\text{g/L}$  (ppb) concentration of sodium dichromate in the reactor cooling water. At an average cooling water usage rate of approximately 30,000~gal/min at each at the three reactors (105-D, 105-DR, and 100-H), consumption was approximately 0.23~kg of sodium dichromate from 0.32~L (0.085~gal) of stock solution per minute per reactor. This led to approximately 467~L (123.4~gal) per day of stock solution, which required one 19,000~L (5,000~gal) railcar every 41~days per reactor. With the presence of two operating reactors at 100-D, more than one railcar per month was required.

Because of the volume of solution transferred, spills and leaks of concentrated liquid solutions of sodium dichromate materials during receiving, handling, and processing activities near the 100-D-12 waste site, 108-D Building, 185-D Building, and the 100-D-56 pipeline likely occurred on a regular basis. Spills and leaks in these areas upstream from the 190 Building are the most likely source of observed Cr(VI) groundwater contamination. Spills of sodium dichromate at cooling water support facilities had the greatest potential for environmental contamination. Decontamination wastes produced in 100-D/H from the reactor were commingled with other liquids and were routed for disposal in various trenches.

Much of the cooling water was discharged directly to the Columbia River through the outfall pipe system. Discharges of cooling water to the ground downstream from the reactor through leaks in retention basins and trenches and cribs typically infiltrated through the vadose zone into the aquifer and eventually discharged to the Columbia River through the groundwater flow system. Figure 1-11 depicts the relative location of the outfall piping.

#### 4.2.2.2 Radionuclides

The principal radionuclides associated with reactor operations that resulted in vadose zone and/or groundwater concerns at 100-D/H are fission/activation products. These products resulted from reactions occurring within the reactor fuel elements and are tritium, uranium-233/234, uranium-235, and uranium-238.

Fission/activation products. Fission/activation products associated with reactor operations include strontium-90, cesium-137, europium-152/154/155, nickel-63, plutonium-239/240, and technetium-99. Other radionuclides associated with reactor operations include americium-241, carbon-14, cesium-134, cobalt-60, neptunium-237, and plutonium-238. All these fission/activation products commonly entered the environment in reactor cooling water contaminated during episodic fuel cladding failures. The post-reactor cooling water system was monitored for signs of failures and contaminated cooling water was redirected to one of the 107-D, 107-DR, or 107-H Retention Basins reserved for this purpose. During routine reactor operations, no single basin was designated to receive the contaminated cooling water, so all three basins received this waste stream, along with discharges to the 116-DR-1&2 trench during the 1967 infiltration test (BNWL-CC-1352). These contaminants were also discharged to the vadose zone at the 105-D, 105-DR, and 105-H Fuel Storage Basins and related cribs during reactor operations.

**Tritium.** Tritium was formed primarily by neutron activation of lithium during reactor operations. Tritium in the southern portion of 100-D is believed to be related to historical releases of tritium at 100-N. Isolated detections of elevated tritium near the 105-D and 105-DR retention basins is

consistent with the expected release of tritium in the contaminated cooling water following fuel cladding failure events.

*Uranium.* The main source of uranium isotopes (uranium-233/234, -235, and -238) is reactor fuel. During fuel failures, uranium entered the cooling water stream. Uranium is also associated with the spent fuel in the fuel storage basins and neutralized, spent acid etch solutions from the 300 Area that was treated at the 183-H Solar Evaporation Basins.

#### 4.2.2.3 Other Contaminants

Other contaminants were identified with various 100-D/H reactor activities and general plant operations. These contaminants are discussed in the following subsections.

**Nitrate, Lead, and Arsenic.** Lead and arsenic are present in the soil largely as a result of pre-Hanford Site agricultural pesticides (i.e. lead arsenate, discussed in Section 4.1). During Hanford operations, the important arsenic sources continued to be pesticides (insect and rat poisons), while the lead sources included shielding, plumbing/solders, and paint. Nitrate may be associated with former agricultural activities, discharge of nitric acid washes/rinses during reactor and support facility decontamination, and human waste discharged to septic systems.

**Total Chromium.** Chromium occurs naturally in the environment and is typically precipitated as a low-solubility hydroxide molecule, Cr(OH)<sub>3</sub>. As such, chromium is not mobile. Elevated levels of chromium in 100-DH is associated with the discharge of sodium dichromate dihydrate (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-2H<sub>2</sub>O), which contains Cr(VI). Cr(VI) ions can also be subject to chemical reduction under moderately reducing conditions, or by reaction with reducing agents such as ferrous iron. Ferrous iron is very effective at reducing Cr(VI) to Cr(III).

**Chloroform.** Chloroform was detected during the spatial and temporal sampling events. The chloroform is generally coincident with the Cr(VI) plumes at low concentrations of several micrograms per liter. No specific source has been identified, but it is a known degradation product of organic compounds. Chloroform most likely originated as a residue from chlorination of cooling water to control microbial growth.

**Decontamination solutions.** During operations and reactor shutdowns, decontamination solutions were used to remove radionuclides from facility equipment and surfaces. These solutions included chromic, citric, oxalic, nitric, sulfamic, and sulfuric acids, sodium carbonate, sodium fluoride and various commercial organic solvents. The spent solutions were typically discharged to trenches, cribs and French drains. They were also occasionally added to cooling water and discharged to the river.

Water treatment chemicals. The following chemicals were used during raw water treatment prior to use in reactor and other plant operations: sodium dichromate, alum, sulfuric acid, and chloride.

**General plant operations.** General plant operations involved the use of PCBs, coal ash, sodium sulfate, tri-sodium phosphate, chromates, gasoline, diesel, commercial organic solvents, oils, and paint.

## 4.3 Vadose Zone Contamination

This section describes the nature (type and concentration) and extent (distribution) of contamination in the vadose zone due to industrial activities related to the operation of three 100-D/H nuclear reactors. The descriptions of soil contamination represent data collected during previous limited field investigations (*Limited Field Investigation Report for the* 

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100-DR-1 Operable Unit [DOE/RL-93-29], Limited Field Investigation Report for the 100-DR-2 Operable Unit [DOE/RL-94-73], Limited Field Investigation Report for the 100-HR-1 Operable Unit [DOE/RL-93-51], and Limited Field Investigation Report for the 100-HR-2 Operable Unit [DOE/RL-94-53]), site closeout sampling, ongoing interim waste site remediation, and the current RI for constituents with concentrations that exceed background soil concentrations.

Vertical profile figures for the RI boreholes and test pits, plus applicable LFI boreholes, show the distribution of contamination in the vadose zone. Only depth discrete soil analytical results are used to illustrate the nature and extent of the preliminary COPCs in these profiles. The profiles provide visual depictions of the analytes relative to background concentrations (if available), sample depths, waste site structures, depths of remedial action, lithology, stratigraphy, and water table depths (if encountered). Within each profile, data collected below the depth of the interim action excavation defines existing conditions at the 17 interim closed-out waste sites identified for additional characterization in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). Radiological data decayed through year 2012 are presented to provide a more direct comparison to data obtained at multiple sampling events. Undetected values are plotted at minimum detectable activity (MDA) for radionuclides or practical quantitation limit (PQL) for chemicals. Figures 2-1 and 2-2 show the locations of the RI boreholes, test pits, and wells. Figure 4-3 shows the groundwater plumes for Cr(VI), nitrate and strontium-90 in the vicinity of the RI waste sites.

Appendix D (Tables 71-100) provides the analytical results for residual contamination at the 17 RI characterization sites. Appendix E summarizes the analytical results for residual contamination at the other 100-D/H closed-out, interim closed-out, and no action waste sites. The closeout verification data reflect soil concentrations used to closeout waste sites according to the interim action RODs. The data presented are from the shallow zone (0 to 4.6 m [0 to 15 ft] bgs) and/or the deep zone >4.6 m (>15 ft) bgs soil concentrations from CVP or RSVP documents. The concentrations typically represent the 95 percent upper confidence limit (UCL) based on the arithmetic mean of the data obtained from statistical sampling. The lateral extent of contamination at waste sites is generally defined by the boundary of the excavated footprint associated with soil remediation (for example, RTD).

Batch leach testing results for the determination of vadose zone  $K_d$  values to support modeling are presented in Chapter 5 and Appendix C (section C.2)and are not included in the vertical profiles. The batch leach testing results obtained from RI boreholes are from the same sample depth intervals as the vertical profiles reported in this chapter.

The following subsections of Section 4.3 present: the soil analyte exclusion process (4.3.1), the waste site vadose zone profiles (4.3.2 to 4.3.18), the RI well soil and sediment results (4.3.19), a discussion of key waste sites currently undergoing interim action (4.3.20), an RPO well soil sampling summary (4.3.21), an evaluation of water addition to wells and boreholes/uncertainty (4.3.22), and a summary of vadose zone nature and extent (4.3.23).

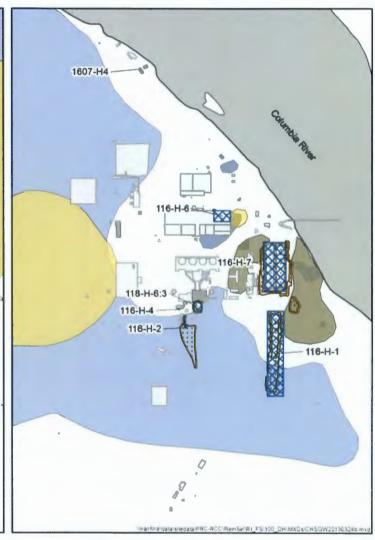


Figure 4-3. Groundwater Plumes in the Vicinity of RI Waste Sites

# 4.3.1 Soil Analytes Excluded

The soil analytical data sets applicable to RI waste site sampling include constituents characterized as having short half-lives (for example, <3 years), common laboratory contaminants, essential nutrients, and essentially nontoxic substances. These constituents are commonly not discussed as detections and are primarily an artifact of the sampling and analysis process, not observed above background concentrations, or not a human health concern (that is, nontoxic) per *Risk Assessment Guidance for Superfund Volume I Human Health Evaluation Manual (Part A): Interim Final* (EPA/540/1-89/002), hereinafter called the risk assessment guide. Table 4-3 lists the 100-D/H soil target analytes excluded from further consideration in this document.

Table 4-3. 100-D/H Soil Analytes Excluded from Further Consideration\*

	Analyte	Exclusion Rationale	Daughters (Half Life)
	Cerium-144	Half-life less than 3 years (284.91 days)	Pr-144m (1.2 min), Pr-144 (17.28 min), and Nd-144 (stable)
	Cesium-134	Half-life less than 3 years (2.065 years)	Ba-134 (stable)
	Cobalt-58	Half-life less than 3 years (70.86 days)	Ni-58 (stable)
	Iron-59	Half-life less than 3 years (44.495 days)	Co-59 (stable)
	Manganese-54	Half-life less than 3 years (312.03 days)	Fe-54 (stable)
	Ruthenium-103	Half-life less than 3 years (39.26 days)	Rh-103m (56.12 min), and Rh-103 (stable)
	Ruthenium-106	Half-life less than 3 years (373.59 days)	Rh-106 (29.9 sec) and Pd-106 (stable)
clides	Sodium-22	Half-life less than 3 years (2.6019 years)	Ne-22 (stable)
Radionuclides	Tin-113	Half-life less than 3 years (115.09 days)	In-113m (1.658 hours) and In-113 (stable)
~	Uranium-240	Half-life less than 3 years (14.1 hours)	Np-240 (7.22 min), and Np-240 (1.03 hours)
	Analyte	Exclusion Rationale	Half Life
	Radium-224	Decay daughter of Thorium-232/ Radium-228; in equilibrium with parent	3.66 days
	Thorium-234	Decay daughter of Uranium-238; in equilibrium with parent	24.1 days
	Actinium-228	Decay daughter of Thorium-232/ Radium-228; in equilibrium with parent	6.15 hours
	Lead-212	Decay daughter of Thorium-232/ Radium-228; in equilibrium with parent	10.64 hours

Table 4-3. 100-D/H Soil Analytes Excluded from Further Consideration\*

	Analyte	Exclusion Rationale	Daughters (Half Life)
	Lead-214 Decay daughter of Radium-226; in equilibrium with parent		26.8 minutes
	Thorium-228	Decay daughter of Th-232/Radium-228; in equilibrium with parent	1.91 years
	Potassium-40	Naturally occurring background radiation	1.25 billion years
	Thorium-230	Only potential source from naturally occurring background radiation (insufficient in growth time for the Hanford Site introduced uranium as decay daughter of Uranium-234)	75.38 thousand years
	Radium-226	Only potential source from naturally occurring background radiation (insufficient in growth time for the Hanford Site introduced uranium as decay daughter of Uranium-234/Thorium-230)	1.6 thousand years
	Radium-228	Decay daughter of Thorium-232. Will be in equilibrium with parent	5.75 years
	Thorium-232	Naturally occurring background radiation	14 billion years
	Analyte	Exclusion Rationale	Half Life
	Calcium	Essential nutrient	NA
	Chloride	Essential nutrient	NA
clides	Iron	Essential nutrient	NA
nucli	Magnesium	Essential nutrient	NA
Nonradionu	Sodium	Essential nutrient	NA
Non	Potassium	Essential nutrient	NA
	Phosphate	Essential nutrient	NA
	Ammonia	No soil toxicity information available	NA
	Zirconium	No soil toxicity information available	NA

Note: Half-life information was taken from the Radiochemistry Society website (RS, 2011).

NA = not applicable

<sup>\*</sup> List is from 100-D/100-H Decision Unit Target Analyte List Development for Soil (WCH-322).

# 4.3.2 100-D-4 Trench Characterization

The 100-D-4 Trench received sludge and effluent in 1953 from the 107-D/DR retention basins. The interim remedial action excavation was to 2.9 m (9.5 ft) bgs, possibly less than the depth of the original bottom of the trench. Because this site only received sludge and effluent over a short time, it is not considered a high-volume liquid waste site, and may not have affected groundwater during operations. The residual contaminants detected during CVP interim close-out sampling included cesium-137, europium-152, strontium-90, uranium-238, Cr(VI), and PCBs (Aroclor-1254 and -1260).

A test pit was excavated through it during the RI (Figure 4-4) to characterize the trench. The soil samples were analyzed to evaluate the vertical extent of contamination in the vadose zone to a depth of 5.8 m (19 ft) bgs. The results of these RI samples and the CVP sample results are presented in Appendix D (Table D-71). The RI test pit results for contaminants detected above background levels and for contaminants detected that do not have background values are presented in Figure 4-5.

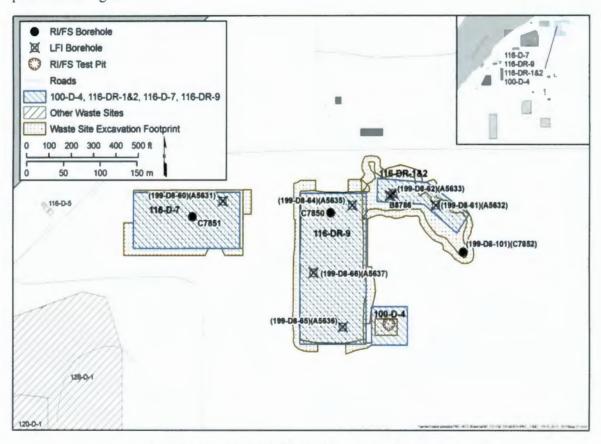


Figure 4-4. 100-D-4, 116-D-7, 116-DR-1 & 2, and 116-DR-9 Location Map

Of the 18 radioactive and 56 non-radioactive contaminants analyzed-for in the RI test pit samples, four were detected or were present above background (see Figure 4-5). Between the CVP and RI results, 11 contaminants were detected above background concentrations in the vadose zone beneath the trench. The detected contaminant concentrations generally decreased with depth, with the exception of strontium (metal) and tin. Only concentrations of Cr(VI) and nitrate reported in nearby groundwater monitoring wells exceeded water quality standards (see Figure 4-3 for groundwater contaminant plume locations). Soil concentrations detected or present above

background levels are compared to soil concentrations protective of groundwater and surface water (i.e., PRGs and soil screening levels [SSLs]) in Chapter 5. The CVP and RI data are also used in Chapter 6 for the human health risk evaluation.

## 4.3.3 116-D-7 Retention Basin Characterization

The 116-D-7 Retention Basin received 105-D Reactor cooling water from 1944-1967. After radioactive decay and thermal cooling, the effluent was discharged to the Columbia River. Due to cooling water leaks and spills, the radionuclide inventory near the basin ranged from 5 to 400 Ci during operations. The basin contamination extended beyond the depth of the interim remedial excavation (7.4 m [24.3 ft]) and reached the water table during operations.

R1 borehole C7851 was drilled (Figure 4-4) and soil samples were collected and analyzed to evaluate contamination in the vadose zone to the depth of the water table (19 m [62.3 ft]) bgs. The 116-D-7 RI borehole C7851, 1992 LFI borehole A5631 (which extended to 11.2 m [36.6 ft] bgs), and the interim closeout CVP data are summarized in Appendix D (Tables D-79, D-80, and D-81). The RI and LFI borehole data for contaminants detected or present above background levels are presented in Figures 4-6, 4-7, and 4-8.

Between the CVP, LFI, and RI sample results for 116-D-7, 21 contaminants were detected or were present in the vadose zone above background levels. The profiles show that higher contaminant concentrations are typically in the upper half of the vadose zone and contaminant concentrations generally decreased with depth, except for tritium and barium. Only concentrations of Cr(VI) and nitrate reported in nearby groundwater monitoring wells exceeded water quality standards (see Figure 4-3 for groundwater contaminant plume locations). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP, LFI, and RI data are also used in Chapter 6 for the human health risk evaluation.

## 4.3.4 116-DR-1&2 Trench Characterization

The 116-DR-1&2 Trench received 40 million L (10.5 million gal) of effluent, 40 kg (88 lb) of sodium dichromate, and a 3.1-curie radiological inventory from 1950-1967. The trench contamination extended beyond the depth of the interim remedial excavation [5.0 m (16.4 ft)] and reached the water table during operations.

An RI borehole C7852 (Well 199-D8-101) was drilled (Figure 4-4) and soil samples were collected and analyzed to evaluate contamination through the vadose zone to the depth of the water table (19.6 m [64.2 ft]) bgs. Previous investigations for this site included three LFI boreholes (A5632, A5633, and B8786) and interim closeout CVP samples. The 116-DR-1&2 Trench RI borehole, previous LFI boreholes, and the CVP data are summarized in Appendix D (Tables D-82 and D-83). Vertical profiles of the RI and LFI borehole results for contaminants detected or present above background levels are presented in Figures 4-9, 4-10, 4-11, 4-12, and 4-13.

An evaluation of the CVP, LFI, and RI sample results for 116-DR-1&2 indicate that 26 contaminants were detected or were present in the vadose zone above background levels. Contaminant concentrations generally decreased with depth. Only concentrations of Cr(VI) and nitrate reported in nearby groundwater monitoring wells exceeded water quality standards (see Figure 4-3 for groundwater contaminant plume locations). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP, LFI, and RI data are also used in Chapter 6 for the human health risk evaluation.

## 4.3.5 116-DR-9 Retention Basin Characterization

The 116-DR-9 Retention Basin received 105-DR Reactor cooling water from 1950 to 1967. After radioactive decay and thermal cooling the effluent was discharged to the Columbia River. Due to cooling water leaks and spills, the radionuclide inventory near the basin ranged from 5 to 400 Ci during operations. The basin contamination extended beyond the depth of the interim remedial excavation (4.75 m [15.6 ft]) and reached the water table during operations.

An RI borehole C7850 was drilled (Figure 4-4) and soil samples were collected and analyzed to evaluate contamination in the vadose zone to the depth of the water table (19.6 m [64.2 ft]) bgs. The 116-D-9 RI borehole C7850, three previous LFI boreholes (A5635, A5636, and A5637), and the interim closeout CVP data are summarized in Appendix D (Tables D-84 and D-85). The RI and LFI borehole data for contaminants detected or present above background levels are presented in Figures 4-14, 4-15, 4-16, 4-17, and 4-18.

Between the CVP, LFI, and RI sample results for this retention basin, 27 contaminants were detected or were present in the vadose zone above background levels. Contaminant concentrations generally decreased with depth, except for carbon-14 and tin (their concentrations generally increased with depth to the water table). Only concentrations of Cr(VI) and nitrate reported in nearby groundwater monitoring wells exceeded water quality standards (see Figure 4-3 for groundwater contaminant plume locations). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP, LFI, and RI data are also used in Chapter 6 for the human health risk evaluation.

## 4.3.6 100-D-12 French Drain Characterization

The 100-D-12 Pumping Station/French Drain received concentrated sodium dichromate (70%) and sulfuric acid solutions during operations. The volume of liquid received and the dates of operation are not well documented for this site; however, it is suspected of being a major source of Cr(VI) for the 100-D south groundwater plume. The interim remedial action excavation was to 2.4 m (7.9 ft), potentially less than the depth of the French Drain structure. The CVP interim closeout sample analysis for 100-D-12 only included Cr(VI).

To ensure the proper placement of the borehole C8668 (Well 199-D5-144), which was prescribed for this site, a test pit was first completed to about 7.6 m (25 ft) bgs to sample the soil and visually inspect the subsurface soils for sodium dichromate staining (Figure 4-19). After establishing the borehole location, the test pit was backfilled and a borehole was drilled to evaluate the vertical extent of contamination in the vadose zone to the water table at 25.9 m (85.1 ft) bgs. The results of the test pit, borehole, and CVP sample results are presented in Appendix D (Tables D-72 and D-73). The RI test pit and borehole results for contaminants detected above background levels and for contaminants detected that do not have background values are also presented in Figure 4-20.

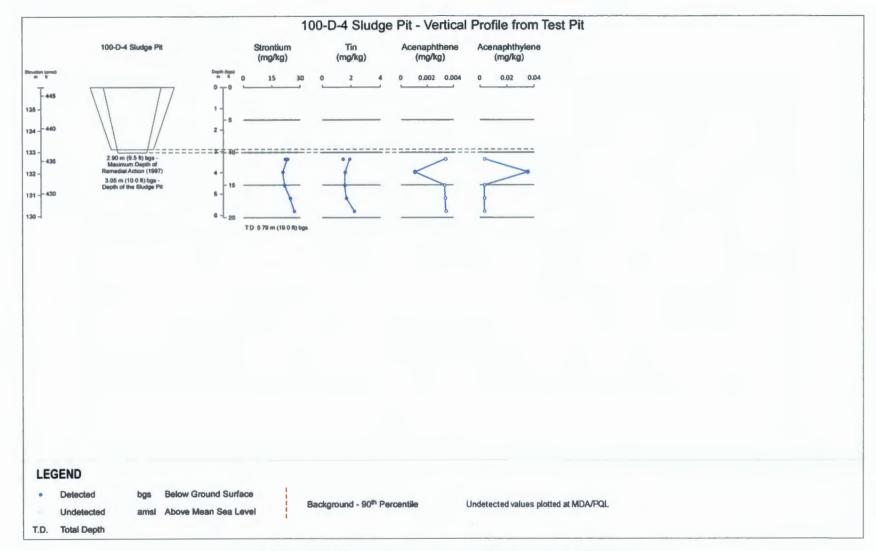


Figure 4-5. 100-D-4 Trench Vertical Profiles of Contamination in Test Pit

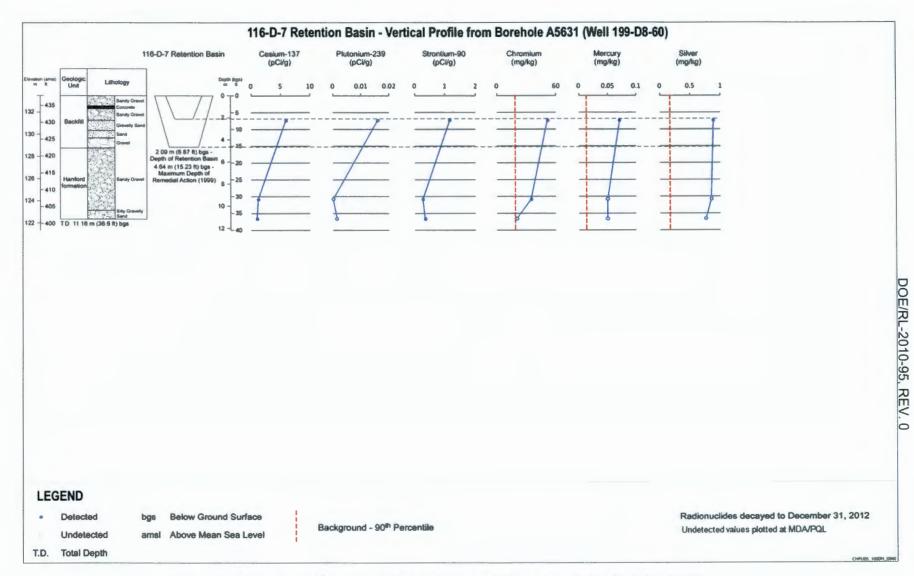
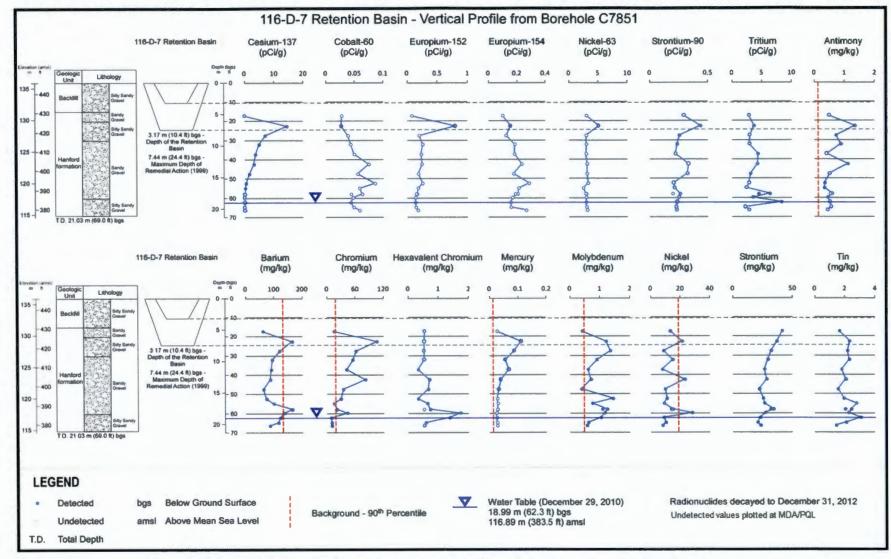


Figure 4-6. 116-D-7 Vertical Profiles of Contamination in LFI Borehole A5631 (Well 199-D8-60)



4-24

Figure 4-7. 116-D-7 Vertical Profiles of Contamination in Remedial Investigation Borehole C7851

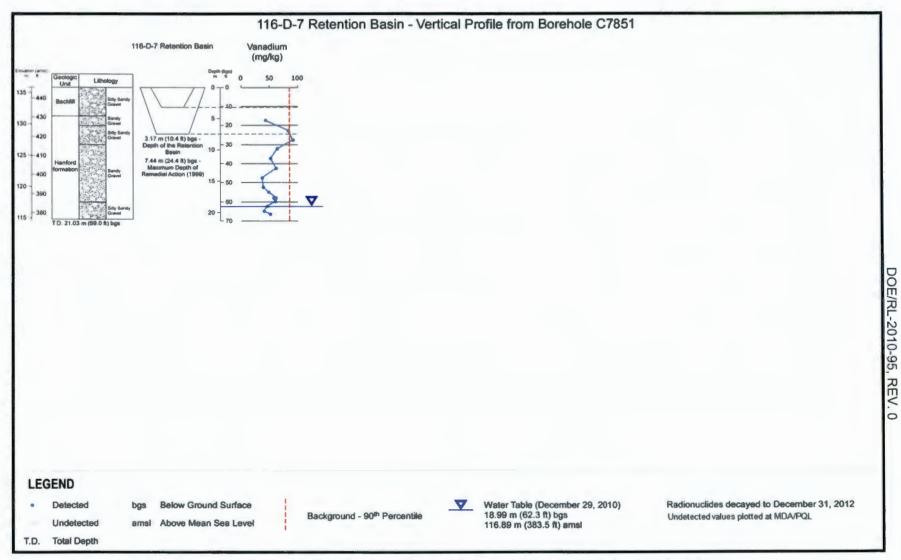


Figure 4-8. 116-D-7 Vertical Profiles of Contamination in Remedial Investigation Borehole C7851

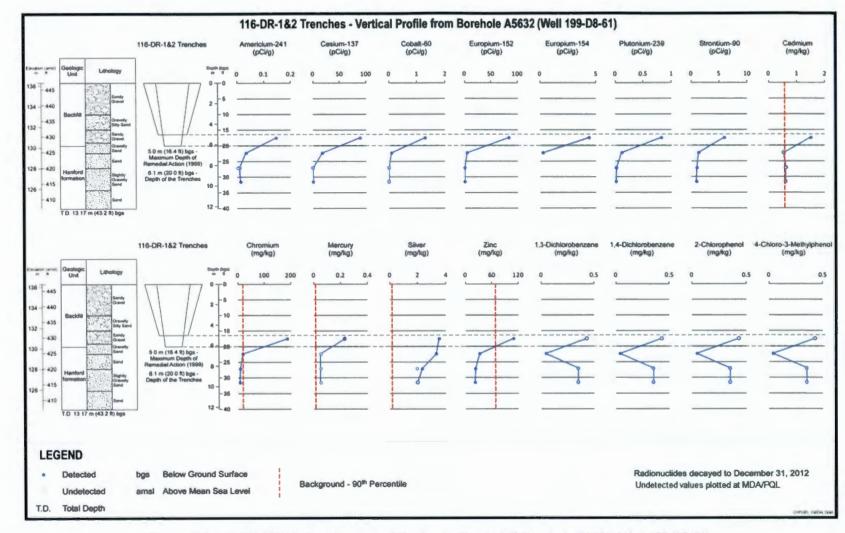


Figure 4-9. 116-DR-1&2 Vertical Profiles of Contamination in LFI Borehole A5632 (Well 199-D8-61)

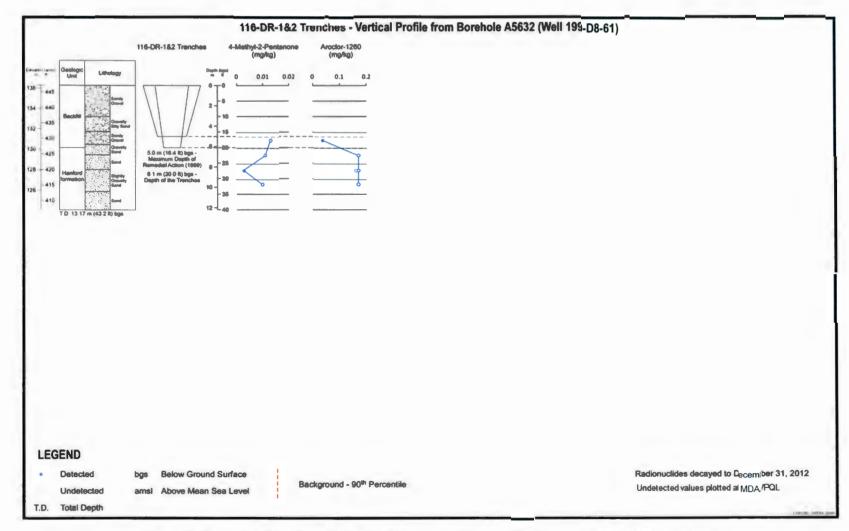


Figure 4-10. 116-DR-1&2 Vertical Profiles of Contamination in LFI Borehole A5632 (Well 199-D8-61)

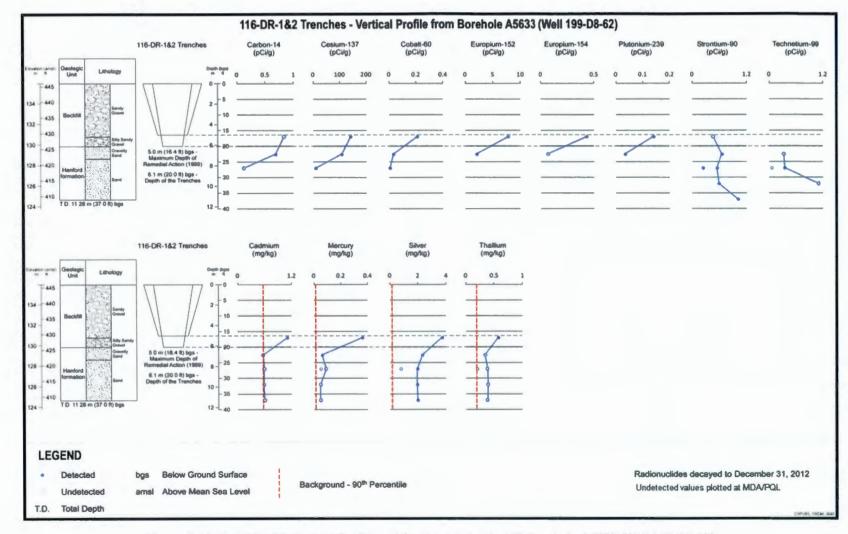


Figure 4-11. 116-DR-1&2 Vertical Profiles of Contamination in LFI Borehole A5633 (Well 199-D8-62)

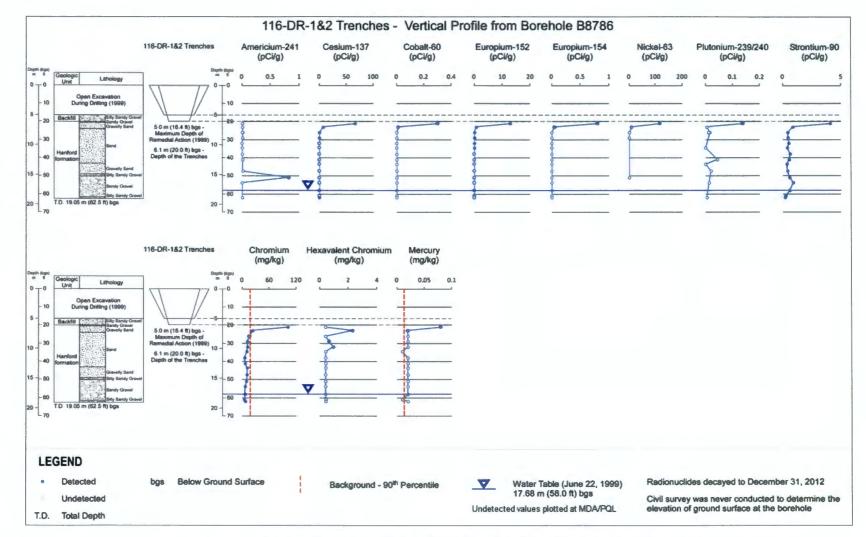
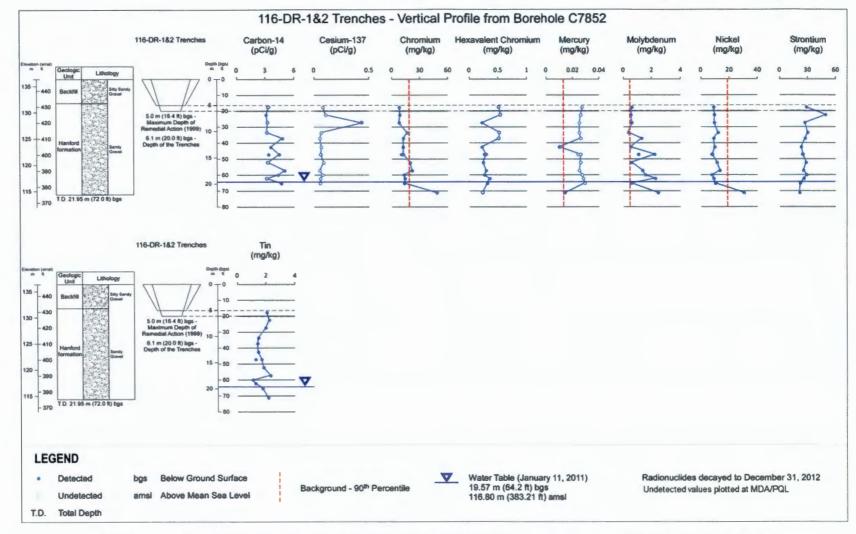


Figure 4-12. 116-DR-1&2 Vertical Profiles of Contamination in Field Remediation Borehole B8786



4-30

Figure 4-13. 116-DR-1&2 Vertical Profiles of Contamination in Remedial Investigation Borehole C7852 (Well 199-D8-101)

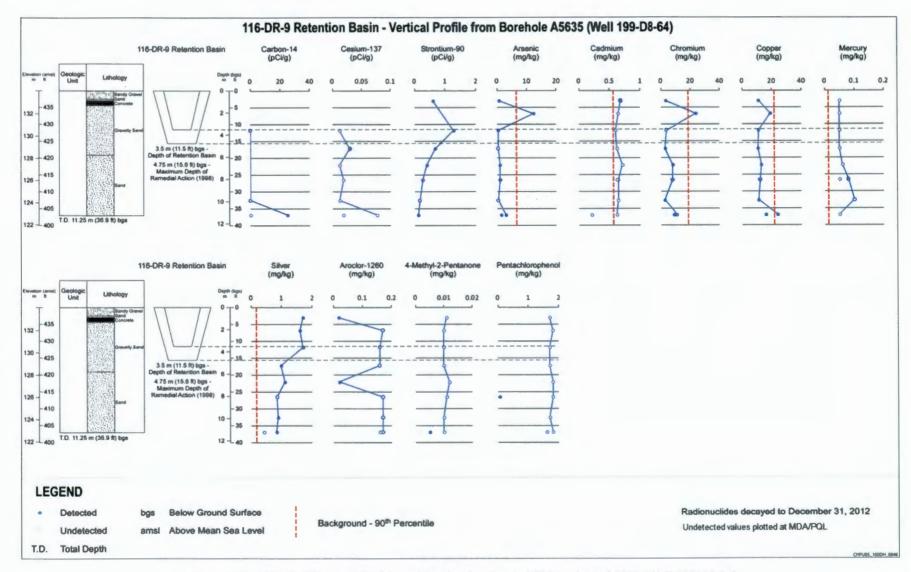


Figure 4-14. 116-DR-9 Vertical Profiles of Contamination in LFI Borehole A5635 (Well 199-D8-64)

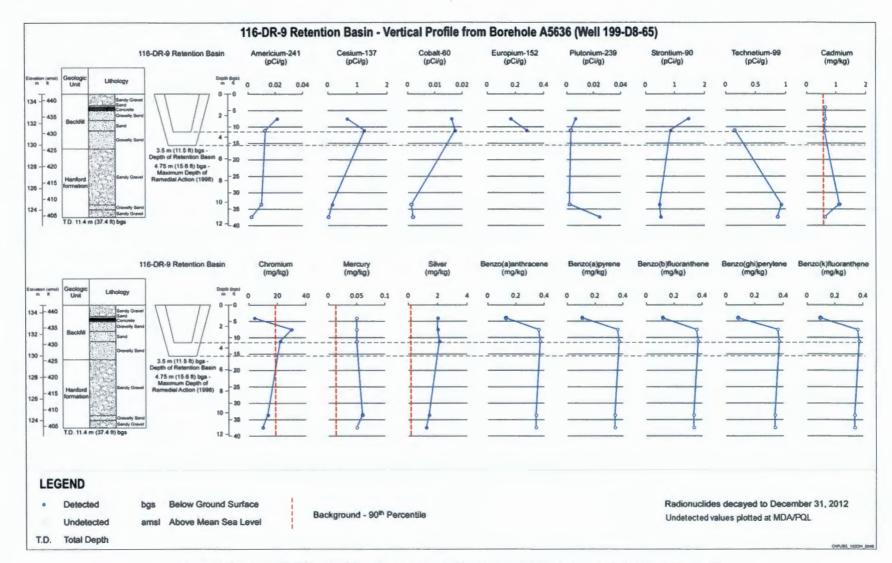


Figure 4-15. 116-DR-9 Vertical Profiles of Contamination in LFI Borehole A5636 (Well199-D8-65)

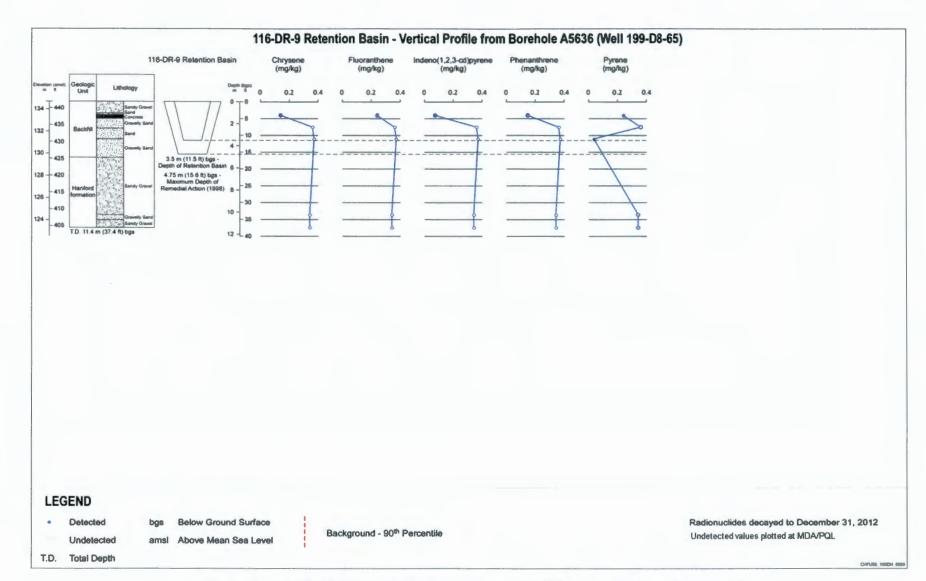
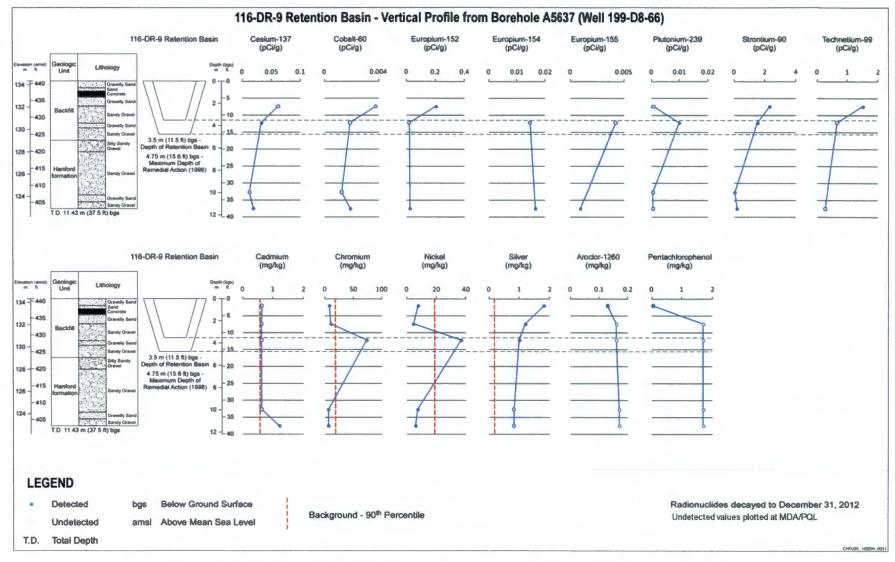


Figure 4-16. 116-DR-9 Vertical Profiles of Contamination in LFI Borehole A5636 (Well 199-D8-65)



4-34

Figure 4-17. 116-DR-9 Vertical Profiles of Contamination in LFI Borehole A5637 (Well 199-D8-66)

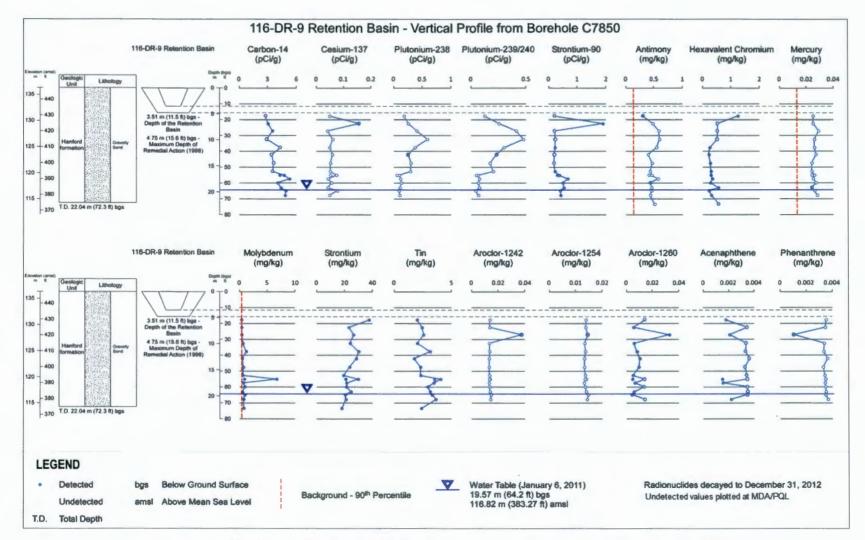


Figure 4-18. 116-DR-9 Vertical Profiles of Contamination in Remedial Investigation Borehole C7850

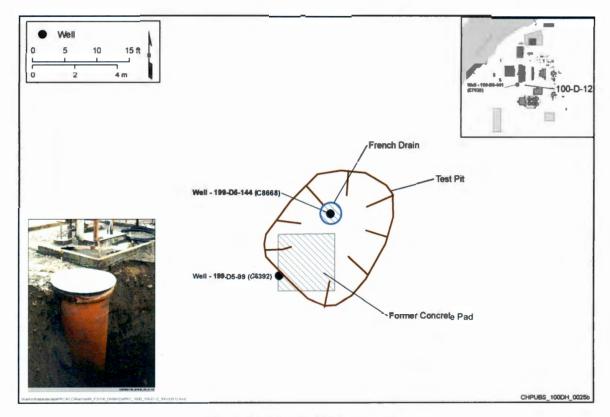


Figure 4-19. 100-D-12 Location Map

Of the 18 radioactive and 56 nonradioactive contaminants analyzed-for in the RI test pit and borehole samples, 10 were detected (see Figure 4-20). Between the CVP and RI results, 10 contaminants, including total chromium and Cr(VI), were detected or were present above background concentrations in the vadose zone beneath the site. Contaminant concentrations generally decreased with depth, except for strontium-90, with its highest concentration (2.2 pCi/g) near the vadose zone-groundwater interface. Only concentrations of Cr(VI) and nitrate reported in nearby groundwater monitoring wells exceeded water quality standards (see Figure 4-3 for groundwater contaminant plume locations). The total chromium and Cr(VI) in the vadose zone at 100-D-12 may be associated with the 100-D-100 waste site, which is being remediated. Prior to the start of interim remedial action at 100-D-100, the waste site boundary was approximately 40 m south of the 100-D-12 Site boundary. Because of the contamination detected during remedial action, the 100-D-100 waste site has been extended north of the 100-D-12 boundary. Additional discussion of the 100-D-100 waste site is presented in Section 4.3.20, Potentially Significant Cr(VI) Waste Sites Undergoing Active Remediation. Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP and RI data are also used in Chapter 6 for the human health risk evaluation.

A second borehole C7625 (Well 199-D5-141) was drilled during the RI ~108 m (355 ft) northwest of 100-D-12 (Figure 4-19) and completed as a well screened in the first water bearing unit of the RUM. Information from this borehole is included here because of its proximity to 100-D-12 and its location about 10 m (32 ft) west of the 100-D-72 waste site (which includes a concrete encasement that protected the service piping for air, steam, filtered water, lime slurry, and sulfuric acid, plus drained acid waste to a neutralization pit). These components were

associated with the storage and flow of sulfuric acid to the 183-D Head House. This borehole was also drilled and samples were collected through the vadose zone to the water table (26 m [85.2 ft] bgs). Appendix D (Table D-103) summarizes the results of the borehole samples and Figure 4-21 presents vertical profiles for contaminants detected and present above background levels. Of the 18 radioactive and 56 nonradioactive contaminants analyzed-for in the borehole samples, eight contaminants were identified in the vadose zone above background concentrations from a depth of 7.6 m (25 ft) bgs to the water table. The maximum tritium concentration was 18.6 pCi/g (at 70 ft bgs), while the maximum total chromium, molybdenum, nickel, and strontium (metal) concentrations are detected about 18.9 m (62 ft) bgs. Only nitrate and Cr (VI) exceed the water quality standards in nearby groundwater monitoring wells within the unconfined aquifer (see Figure 4-3), with nitrate concentrations fluctuating between slightly above and slightly below the standard. Contamination was not identified in the first water bearing unit of the RUM. Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5.

## 4.3.7 100-D-56:1 Pipeline Characterization

The 100-D-56:1 Pipeline is an abandoned 7.6 cm (3 in.) diameter underground chemical supply line that was used from 1944 to 1950. The pipeline transported sodium silicate and sodium dichromate liquids between the 108-D, 185-D, and 190-D buildings. During remedial action 1,500 L (400 gal) of sodium dichromate was removed from the pipeline and a hole was noted at a 90-degree bend in the pipeline. The pipeline interim remedial action excavation was to 2 m (6.6 ft) bgs.

RI borehole C8375 (Well 199-D-143) was needed to better define the vertical extent of contamination at the leak location (Figure 4-22). The borehole was drilled and samples were collected through the vadose zone to the water table (25.1 m [82.5 ft] bgs). The results of the borehole and interim closeout CVP samples are presented in Appendix D (Tables D-74 and D-75), while the interim closeout CVP sample results for 100-D-56:1 are in Appendix E (Table E-1). The RI borehole results for contaminants detected above background levels and for contaminants detected that do not have background values are also presented in Figure 4-23.

Of the 18 radioactive and 56 nonradioactive contaminants analyzed-for in the borehole samples, seven were detected (Figure 4-23). Between the CVP and RI results, 16 contaminants were detected or were present above background concentrations in the vadose zone beneath the site. While Cr(VI) was not detected in the borehole results, it was measured to a depth of 2 m (6.6 ft) in the CVP results. The greatest concentrations of strontium-90, total chromium, lithium, molybdenum, and strontium (metal) were detected 50 to 70 ft bgs in the vadose zone. Only nitrate and Cr(VI) exceeded drinking water standards in nearby groundwater monitoring wells (Figures 4-2 and 4-3 for well locations). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP and RI data are also used in Chapter 6 for the human health risk evaluation.

During the RI, a second borehole C7866 (Well 199-D5-140) was drilled near the origin of the 100-D-56:1 pipeline, within the 100-D-101 waste site boundary, which includes the soil beneath the 108-D Chemical Pump House (Figure 4-22). This borehole was also drilled and samples were collected through the vadose zone to the water table (25.1 m [82.5 ft] bgs). The results of the borehole samples are summarized in Appendix D (Table D-112) and Figure 4-24 presents vertical profiles for contaminants detected and present above background levels. Of the 18 radioactive and 56 nonradioactive contaminants analyzed-for in the borehole samples, seven contaminants

were detected or were present above background concentrations in the vadose zone from 5 m (16 ft) bgs to the water table 25.8 m (84.7 ft) bgs. The maximum total chromium, molybdenum, and nickel concentrations are detected about 24.6 m (81 ft) bgs. Other contaminant trends varied, but generally decreased with depth and are typically low concentration single detections (i.e., mercury) above background. Only nitrate and Cr (VI) exceed drinking water standards in nearby groundwater monitoring wells (see Figures 4-2 and 4-3 for well locations). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5.

### 4.3.8 116-D-1A Trench Characterization

The 116-D-1A Trench received 200,000 L (52,834 gal) of FSB effluent and sludge from 1947 to 1952. This material contained 1,000 kg (2,200 lb) sodium dichromate and a radiological inventory of 4.7 curies. The site is categorized as a low-volume, high-concentration liquid waste site that was not expected to affect groundwater during operations. The interim action excavation to 4.6 m (15 ft) bgs was potentially less than the depth of the original trench, (see appendix E, Table E-1) so a residual source of contamination may remain in the vadose zone that could affect groundwater quality. An RI borehole C7622 (Well 199-D5-132) was drilled (Figure 4-22) and soil samples were collected and analyzed to evaluate the extent of contamination through the vadose zone to the water table (26 m [85.5 ft] bgs). The borehole data plus interim closeout CVP and LFI data (borehole A5567) for 116-D-1A are summarized in Appendix D (Table D-76). Vertical profiles of RI and LFI borehole data for contaminants detected and present above background levels are also presented in Figures 4-25, 4-26, and 4-27.

Between the CVP, LFI, and RI sample results for 116-D-1A, 26 contaminants were detected or were present above background levels. The profiles show that contaminant trends vary at this site; however, higher concentrations are generally in the upper half of the vadose zone. An exception to the typical contaminant distribution at this site involves the arsenic concentration (167 mg/kg) at the groundwater-vadose zone interface while the other arsenic concentrations were below background values. This arsenic concentration is considered an outlier that is not representative of arsenic concentrations at 116-D-1A because four batch leach samples collected from the same interval had concentrations that were < 2 mg/kg (see Appendix C for the batch leach result summary). Only nitrate, Cr(VI), and strontium-90 exceeded drinking water standards in nearby groundwater monitoring wells (see Figure 4-3). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP, LFI, and RI data are also used in Chapter 6 for the human health risk evaluation.

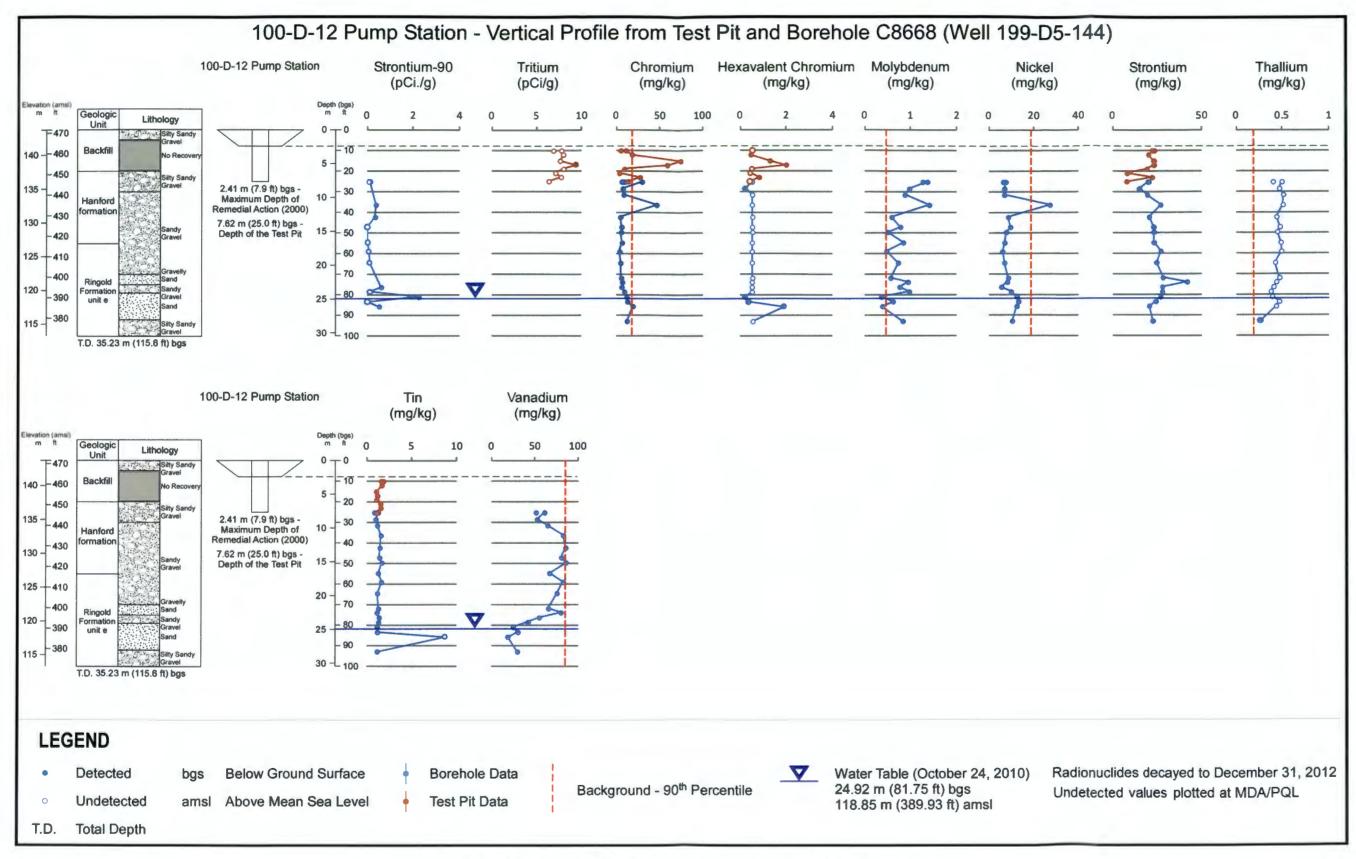


Figure 4-20. 100-D-12 Vertical Profile of Contamination in Borehole C8668 (Well 199-D5-144)

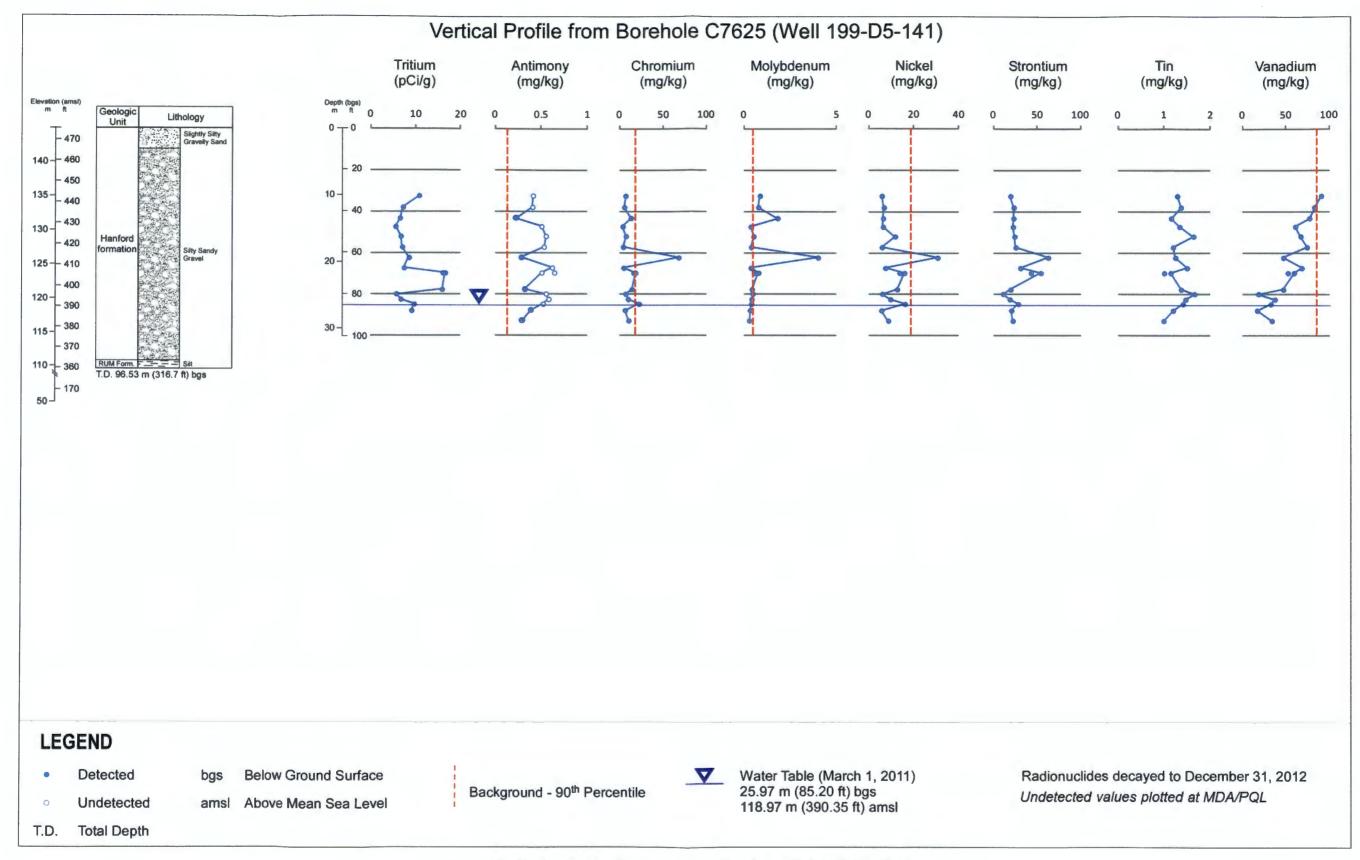


Figure 4-21. Vertical Profile of Contamination in Borehole C7625 (Well 199-D5-141).

Figure 4-22. 100-D-56:1, 116-D-1A, 116-D-1B, 116-D-4, and 118-D-6:3 Location Map

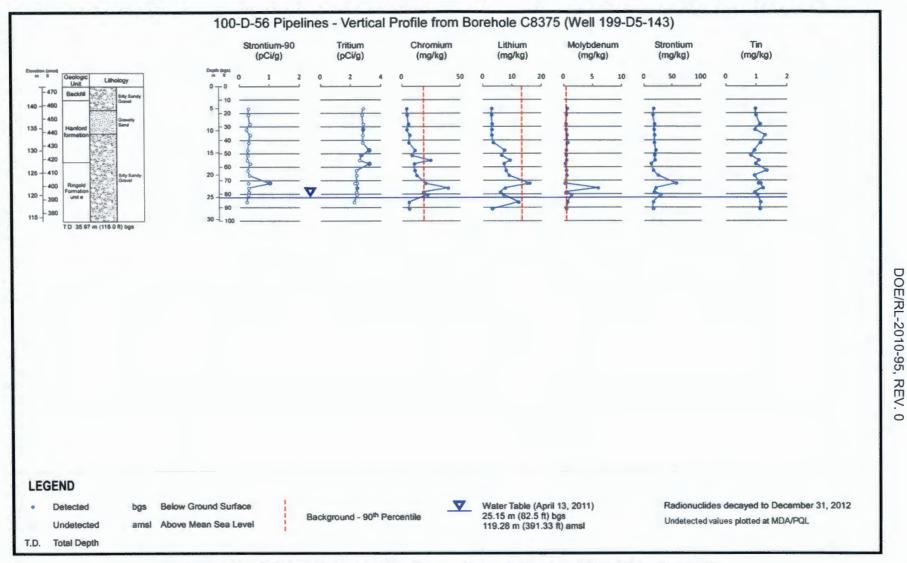


Figure 4-23. 100-D-56:1 Vertical Profile of Contamination in Borehole C8375 (Well 199-D5-143)

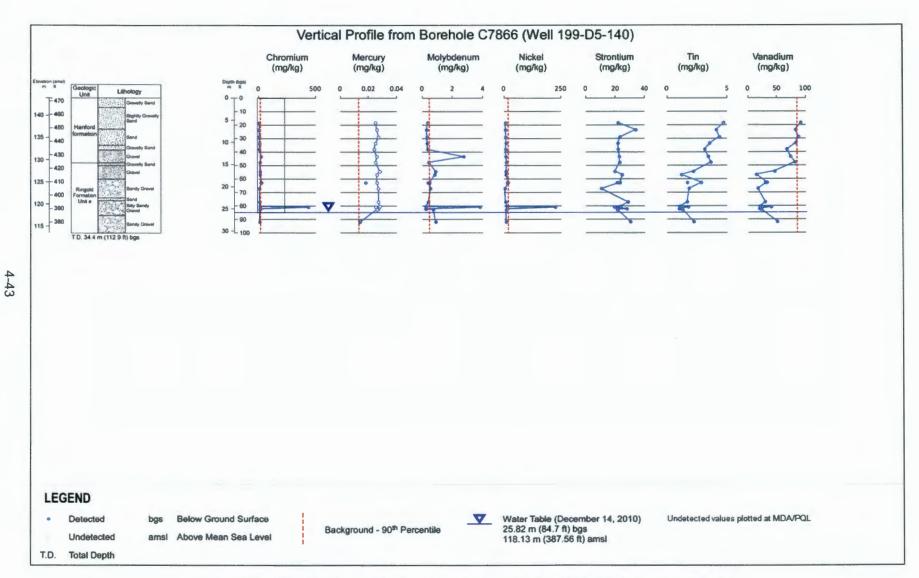


Figure 4-24. 100-D-101 Vertical Profile of Contamination in Borehole C7866 (Well 199-D5-140).

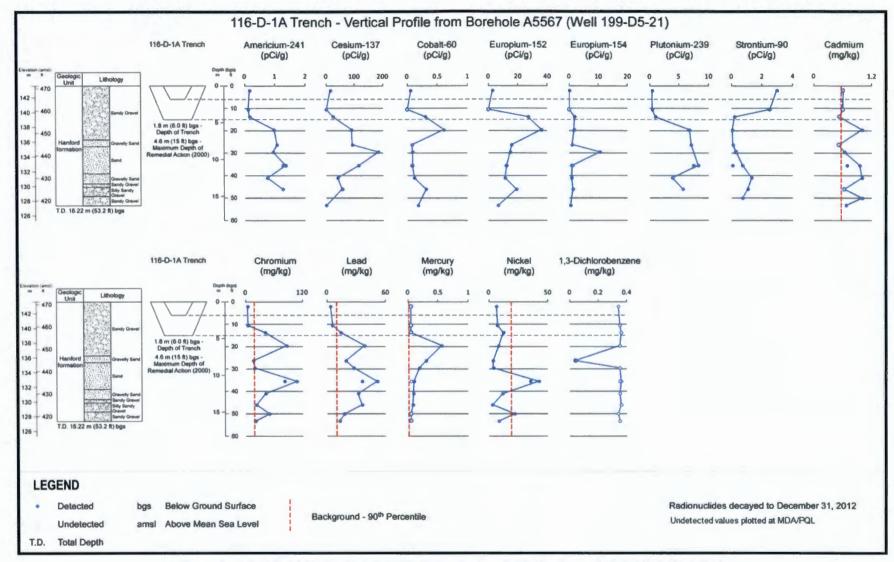


Figure 4-25. 116-D-1A Vertical Profiles of Contamination in LFI Borehole A5567 (Well 199-D5-21)

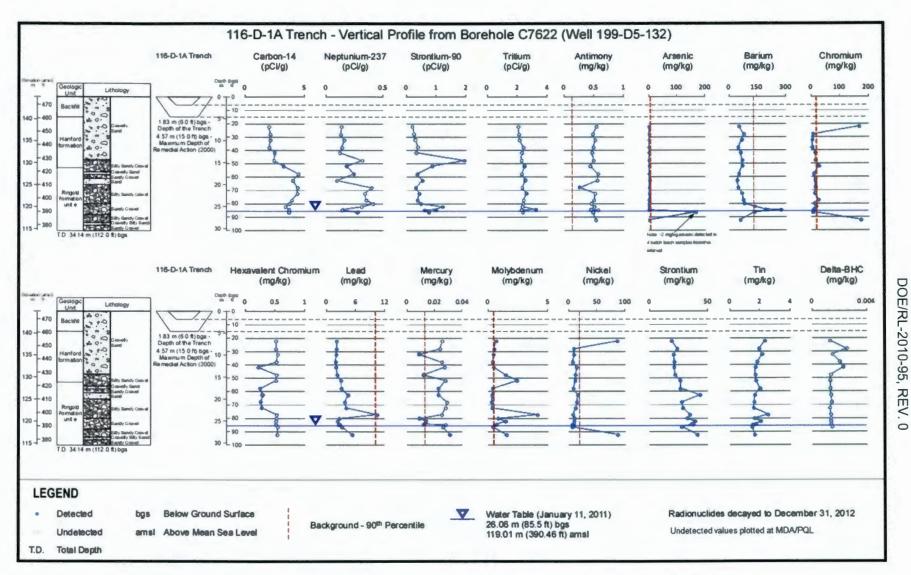


Figure 4-26. 116-D-1A Vertical Profiles of Contamination in RI Borehole C7622 (Well 199-D-5-132)

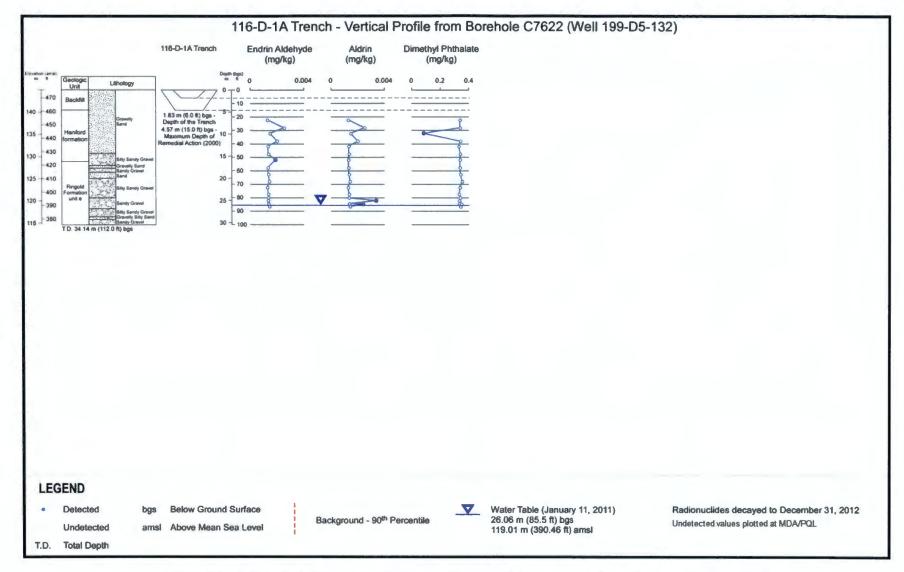


Figure 4-27. 116-D-1A Vertical Profiles of Contamination in Remedial Investigation Borehole C7622 (Well 199-D5-132)

### 4.3.9 116-D-1B Trench Characterization

The 116-D-1B Trench received 8,000,000 L (2,113,376 gal) of sludge and effluent from the FSB from 1953-1967. The effluent and sludge had a 2.6-curie radiological inventory. The trench was a high-volume liquid waste site and the contamination affected the vadose zone groundwater during operations. The interim action excavation to 4.6 m (15 ft) bgs was potentially less than the depth of the original trench, so a residual source of contamination may remain in the vadose zone that could affect groundwater quality.

An RI borehole C7855 was drilled (Figure 4-22) and soil samples were collected and analyzed to evaluate the extent of contamination through the vadose zone to the water table (26.5 m [86.9 ft]) bgs. The RI borehole data plus interim closeout CVP and LFI data for 116-D-1B are summarized in Appendix D (Table D-77). Vertical profiles of the RI and LFI borehole (A5575) data for contaminants detected and present above background levels are also presented in Figures 4-28, 4-29, 4-30, and 4-31.

The combined RI, CVP, and LFI sample results indicate that 45 contaminants were detected or were present above background concentrations beneath 116-D-1B. The profiles show that contaminant trends vary, with higher concentrations generally present in the upper half of the vadose zone. However, total chromium, barium, molybdenum, and delta-BHC have elevated concentrations near the water table. Only nitrate, strontium-90, and Cr(VI) exceed drinking water standards in nearby groundwater monitoring wells (see Figure 4-3). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP, LFI, and RI data are also used in Chapter 6 for the human health risk evaluation.

#### 4.3.10 116-D-4 Crib Characterization

The 116-D-4 Crib received 30,000 L (7,925 gal) of decontamination fluids, solvents and low-level fission products from the 108-D Building from 1956-1967. The interim remedial excavation to 2.8 m (9 ft) bgs for this low-volume waste site was potentially less than the depth of the crib structure. However, only Cr(VI) was detected at the excavation depth in the interim closeout CVP sampling effort.

An RI test pit was excavated (Figure 4-22) and soil samples were collected and analyzed to evaluate the extent of contamination to a depth of 5.8 m (19 ft) bgs. An earlier LFI borehole (A5570) was drilled to 7 m (23 ft) to investigate this site. The test pit, CVP, and LFI data for 116-D-4 are summarized in Appendix D (Table D-78). Vertical profiles of the test pit and LFI borehole data for contaminants detected and present above background levels are also presented in Figures 4-32 and 4-33.

Between the CVP, LFI, and RI sample results for 116-D-4, 11 contaminants were detected or were present in the vadose zone above background levels. Contaminant concentrations generally decreased with depth beneath the site and only nitrate and Cr(VI) exceeded drinking water standards in nearby groundwater monitoring wells (see Figure 4-3). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The CVP, LFI, and RI data are also used in Chapter 6 for the human health risk evaluation.

### 4.3.11 118-D-6 Reactor Fuel Storage Basin Characterization

The 118-D-6 Reactor FSB stored irradiated fuel elements from 1944 to 1967. The cooling water was not removed from the basin until 1985. During interim remedial action, the floor and walls of the basin were left in place, limiting the depth of excavation to less than the engineered structure. Only concrete samples from the FSB floor were collected during the interim closeout CVP effort. Soil samples were not collected from beneath the basin floor, which reportedly leaked during operations.

An RI borehole C7857 (Well 199-D5-142) was drilled adjacent to the FSB (Figure 4-22) and soil samples were collected and analyzed to evaluate vadose zone contamination to the depth of the water table (25 m [82.2 ft]) bgs. The borehole data are summarized in Appendix D (Table D-86). The concrete CVP sample results are not included in Appendix D (Table D-88). The RI borehole data for contaminants detected or present above background levels are presented in Figures 4-34 and 4-35.

The RI results for the FSB indicate that 19 contaminants were detected or were present in the vadose zone above background levels. Most contaminant concentrations generally decreased with depth. However, barium, total chromium, molybdenum, and nickel had their highest concentrations between 60 and 80 ft bgs. Only nitrate, strontium-90, and Cr(VI) are in nearby groundwater wells in excess of drinking water standards (see Figure 4-3). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The RI data are also used in Chapter 6 for the human health risk evaluation.

# 4.3.12 116-H-1 Trench Characterization

The 116-H-1 Trench received effluent from the 116-H-7 retention basin during reactor fuel element failure shut downs from 1952 to 1965 and. The trench received 90,000,000 L (24,000,000 gal) of effluent that included 90 kg (41 lb) of sodium dichromate and a radiological inventory of 33 Ci. The effluent reached the water table during operations, and contamination extended beyond the depth of the interim remedial excavation (4.6 m [15 ft] bgs). The trench is located near the 100-H strontium-90 plume.

An RI borehole (C7864) was drilled adjacent to the trench (Figure 4-36) and soil samples were collected and analyzed to evaluate the vertical extent of vadose zone contamination to the water table (13.3 m [43.5 ft] bgs). In addition, LFI and excavation boreholes A5724 (Well 199-H4-58) and SPC-TW-25 (C3048), respectively) were drilled historically (1992 and 2000, respectively). The CVP, LFI, and RI data are summarized in Appendix D (Tables D-87 and D-88). The RI and LFI borehole data for contaminants detected or present above background levels are presented in Figures 4-37, 4-38, 4-39, 4-40 and 4-41.

The CVP, LFI, and RI analytical results for the 116-H-1 Trench indicate that 43 contaminants were detected or were present in the vadose zone above background levels. Contaminant concentrations generally decreased with depth. However, higher concentrations of antimony, total chromium, copper, lead, and molybdenum were present near the water table. Only Cr(VI) and strontium-90 are in nearby groundwater wells in excess of drinking water standards (see Figure 4-3). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The RI data are also used in Chapter 6 for the human health risk evaluation.

# 4.3.13 116-H-7 Retention Basin Characterization

The 116-H-7 Retention Basin received cooling water from the 105-H Reactor from 1949 to 1965. After radioactive decay and thermal cooling, the effluent was discharged from this concrete basin to the river. The basin, a high-volume liquid site that leaked, affected groundwater during operations and, thus, contamination extended beyond the CVP interim remedial excavation depth (4.75 m [15.6 ft) bgs.

An RI borehole (199-H4-83, C7861, Figure 4-36) was drilled and sampled to evaluate the vertical extent of contamination through the vadose zone to the water table (10.7 m [35 ft]) bgs. Summary data for the CVP, LFI borehole, and RI borehole are presented in Appendix D (Tables D-94, D-95, and D-96). Vertical profiles of borehole contamination detected or present above background are in Figures 4-42 and 4-43.

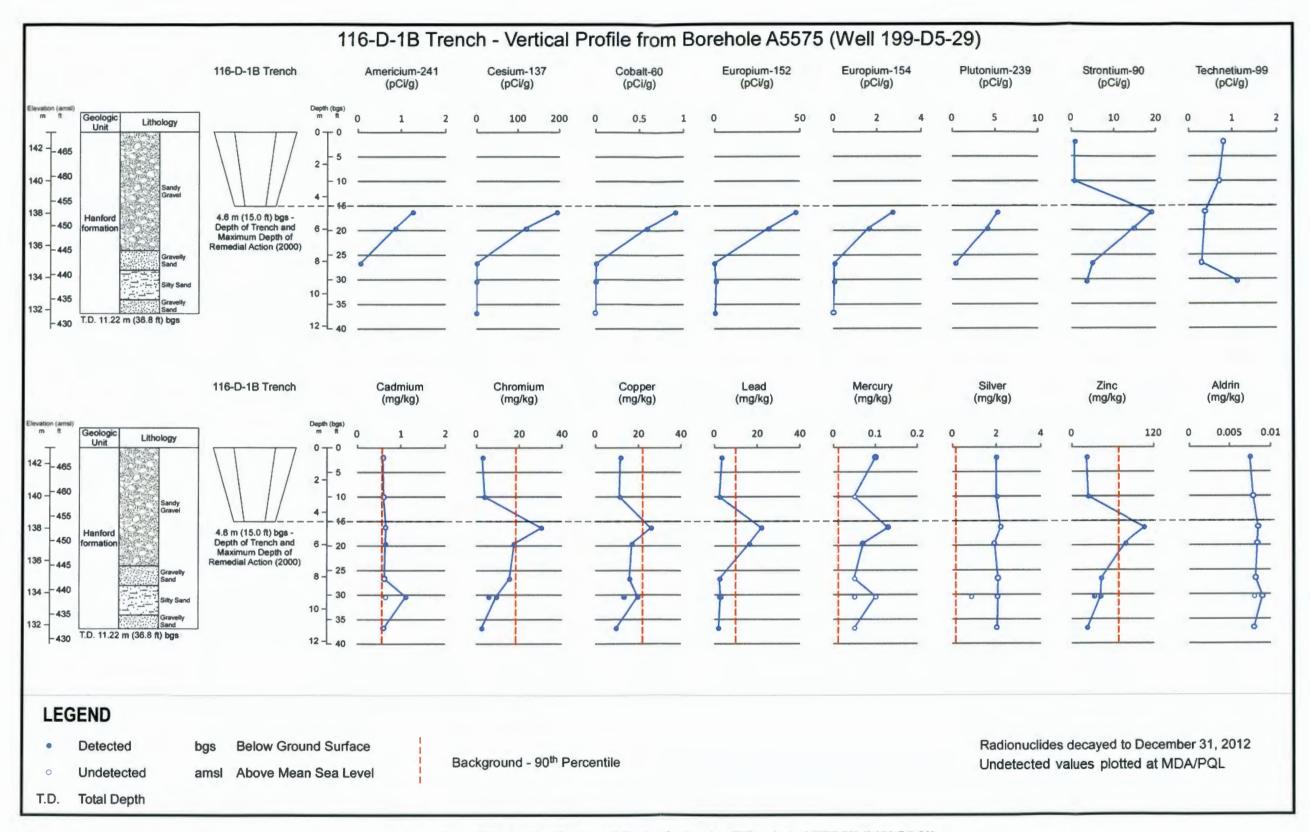


Figure 4-28. 116-D-1B Vertical Profiles of Contamination in LFI Borehole A5575 (Well 199-D5-29)

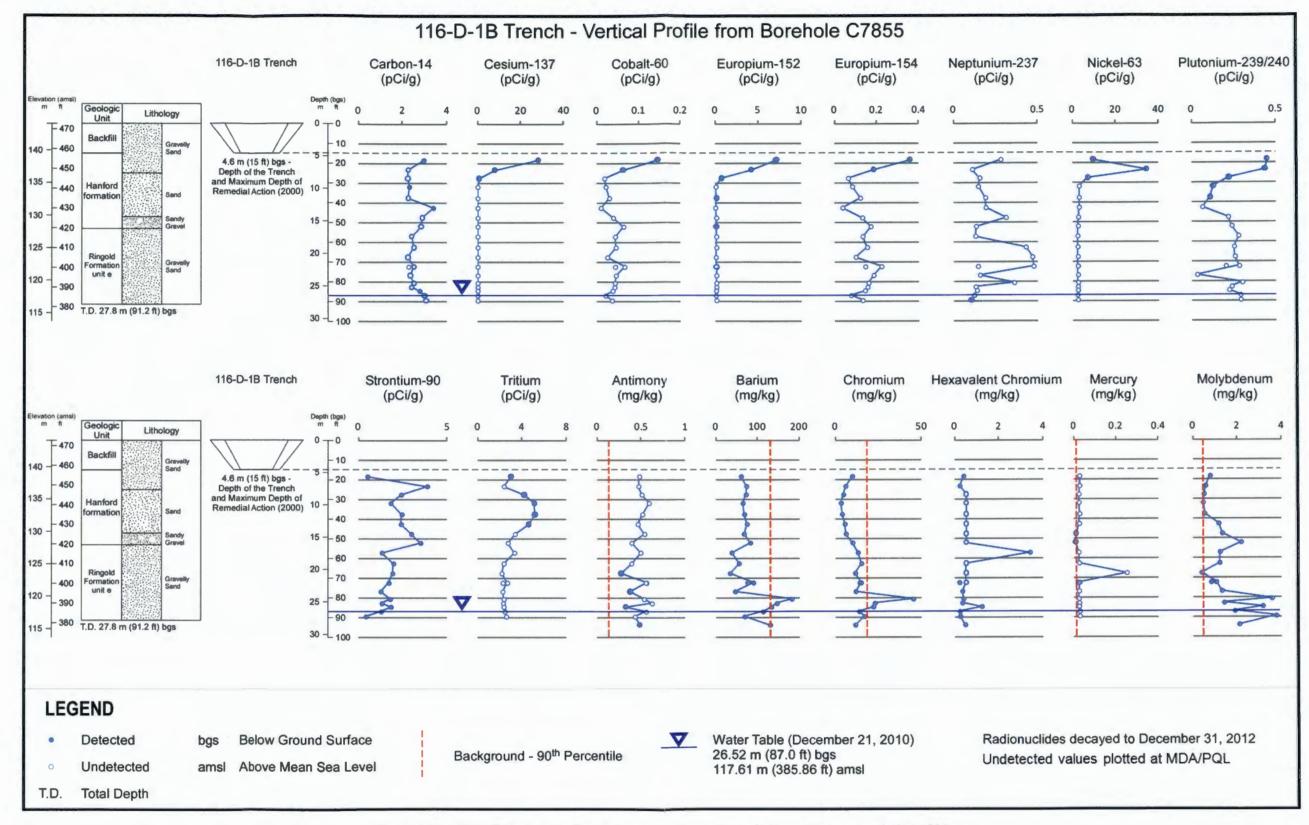


Figure 4-29. 116-D-1B Vertical Profiles of Contamination in Remedial Investigation Borehole C7855

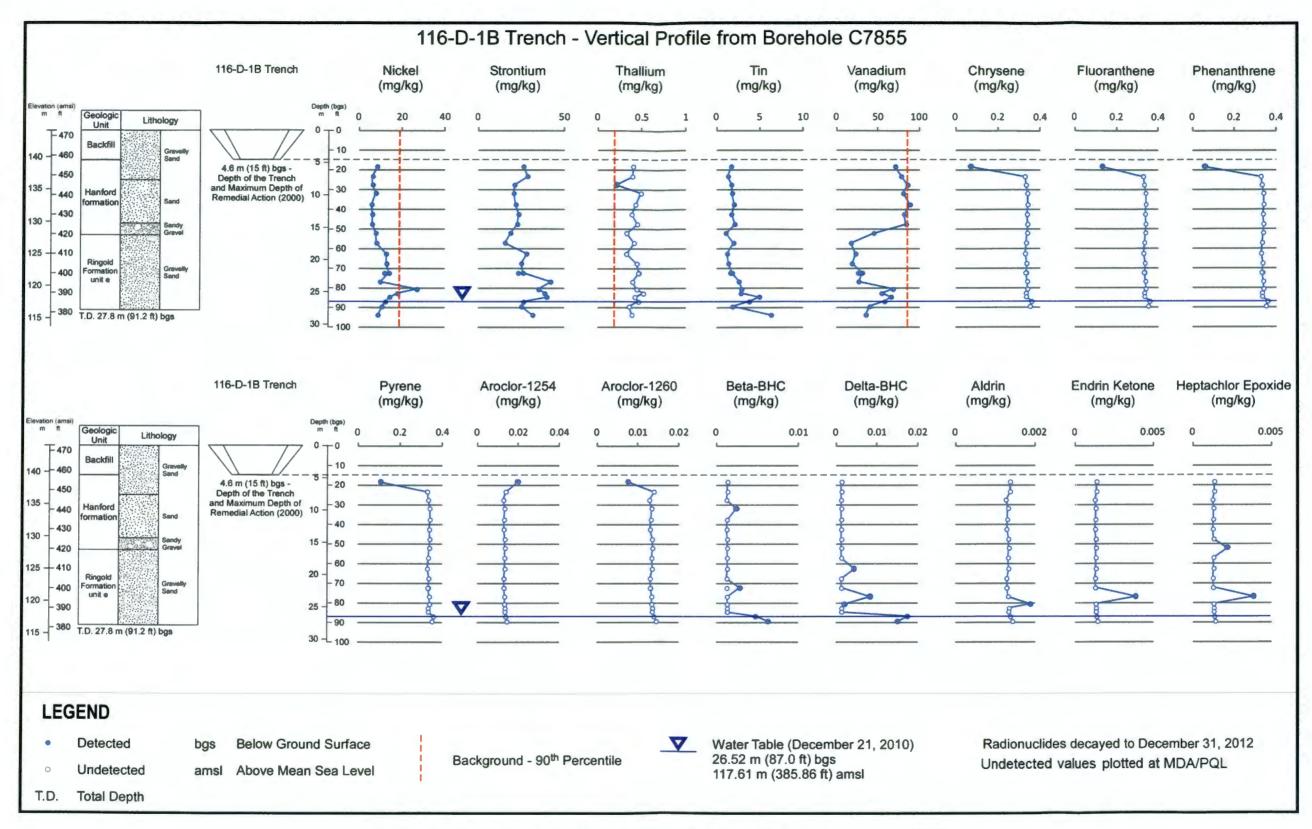


Figure 4-30. 116-D-1B Vertical Profiles of Contamination in Remedial Investigation Borehole C7855

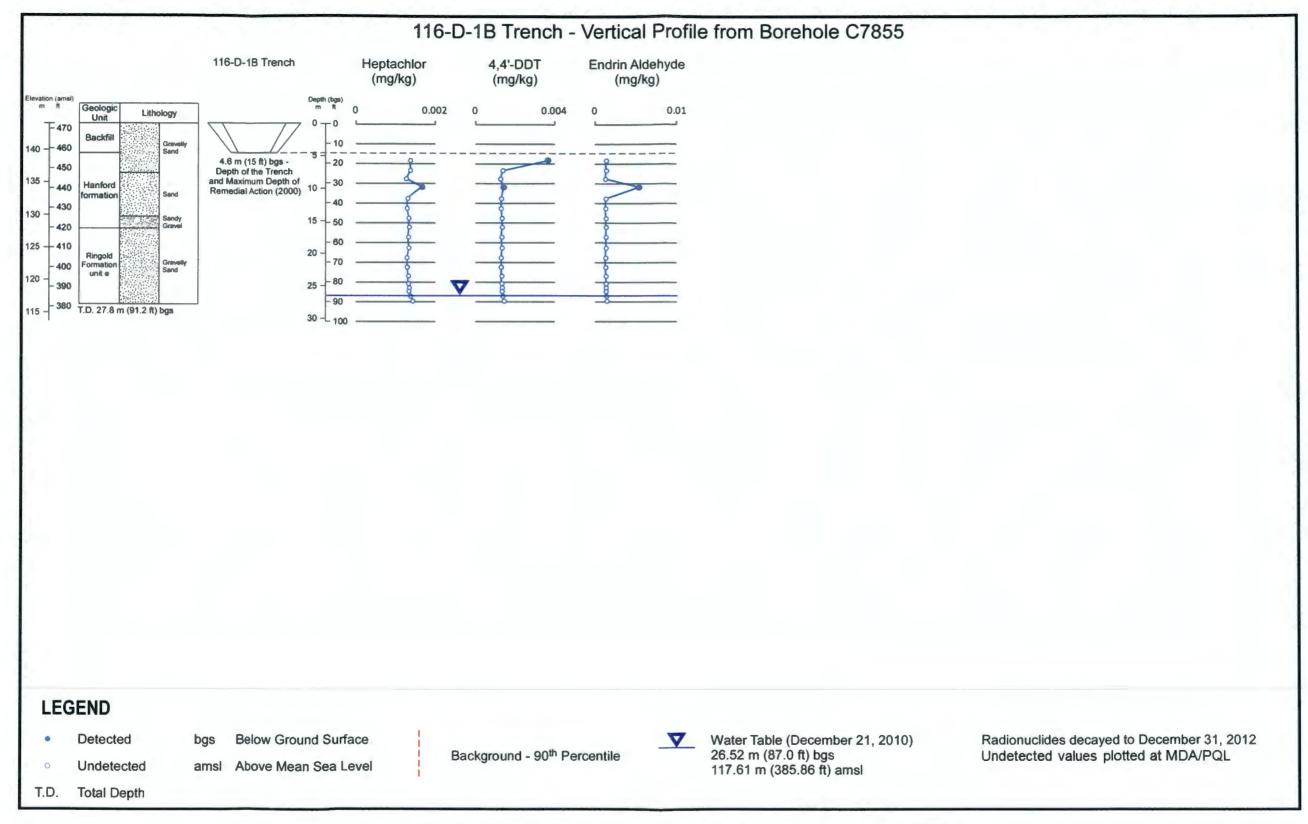


Figure 4-31. 116-D-1B Vertical Profiles of Contamination in Remedial Investigation Borehole C7855

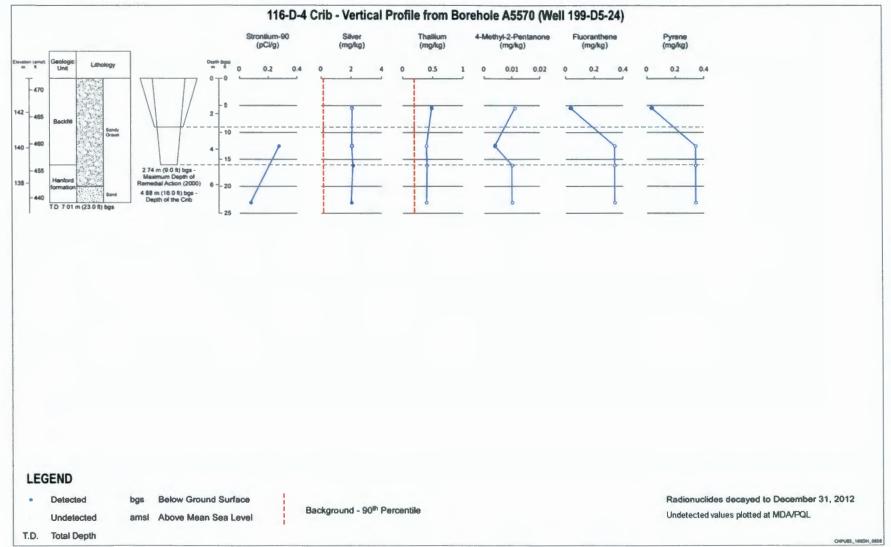


Figure 4-32. 116-D-4 Vertical Profiles of Contamination in LFI Borehole A5570 (Well 199-D5-24)

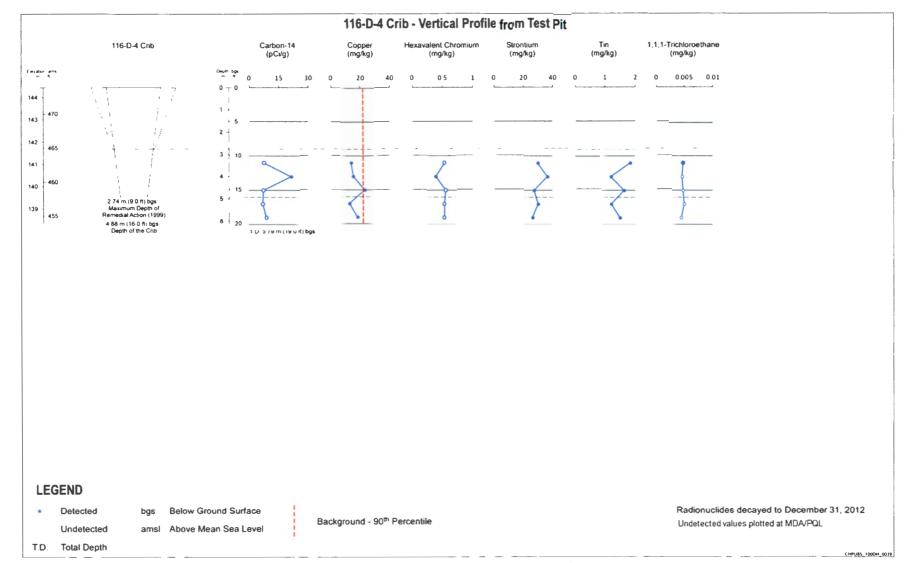


Figure 4-33. 116-D-4 Vertical Profiles of Contamination in Remedia Investigation Test Pit 116-D-4

The CVP, LFI, and RI analytical results for 116-H-7 indicate that 21 contaminants were detected or present above background in the vadose zone beneath the site. Contaminant trends vary at this site with many concentrations generally decreasing with depth. However, strontium-90, antimony, strontium (metal), and molybdenum have increased concentrations toward the water table. Only nitrate and Cr(VI) are detected in nearby groundwater wells in excess of drinking water standards (see Figure 4-3). Observed concentrations of Cr(VI) and strontium-90 in groundwater (Section 4.5.1.1 and 4.5.2), including Cr(VI) in aquifer tube C7650, may reflect contaminant impacts from the 116-H-7 Retention Basin and other waste sites during operations.

Four other contaminants (methyl methacrylate, tetrachloroethylene, trichloroethylene, and bis(2-ethylhexyl) phalate) have had a single detection with very low concentrations (less than 1.2  $\mu$ g/L and flagged as estimated values) in aquifer tube C7650, all associated with two samples collected in 2010. Bis(2- ethylhexyl) phalate was also detected at low levels in 1989 in Well 199-H4-11 (23  $\mu$ g/L), in 2005 in Well 199-H4-13(4  $\mu$ g/L), and in aquifer tube C7549 in 2010 (1.2  $\mu$ g/L); however, it should be noted that this compound is a common laboratory contaminant. There were no other detections in groundwater in the vicinity of 116-H-7. In addition, these contaminants were not detected in vadose zone material from upgradient waste sites. Chapter 5 compares soil concentrations detected or present above background to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL). The RI data are also used in Chapter 6 for the human health risk evaluation.

### 4.3.14 116-H-2 Trench Characterization

The 116-H-2 Trench received effluent from the 105-H Reactor and the 1608-H Pump House from 1950 to 1965. The trench received 600,000,000 L (160,000,000 gal) of effluent that included 600 kg (273 lb) of sodium dichromate and had a radiological inventory of 1.4 Ci. This trench is a high-volume liquid waste site that extends beyond the depth of the interim remedial excavation [2.6 m (8.5 ft) and likely affected groundwater quality during operations.

An RI test pit was excavated through the trench location (Figure 4-44) and soil samples were collected and analyzed to evaluate the vertical extent of contamination to a depth of 5.8 m (19 ft). The CVP, LFI, and RI data are summarized in Appendix D (Table D-89). The RI and LFI borehole A5725 data for contaminants detected or present above background levels are presented in Figures 4-45 and 4-46.

Between the CVP, LFI, and RI sample results for this trench, 12 contaminants were detected or were present above background levels in the vadose zone. Only Cr(VI) was detected in groundwater wells in excess of drinking water standards (see Figure 4-3). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The RI data are also used in Chapter 6 for the human health risk evaluation.

#### 4.3.15 116-H-4 Crib Characterization

The 116-H-4 Crib received effluent from the 105-H Reactor from 1950 to 1952, and the 1,000 L (254 gal) of effluent received included 1,000 kg (454 lb) of sodium dichromate and had a radiological inventory of 270 Ci. Contaminated material was removed from this site in 1960 and placed in the 118-H-5 Burial Ground to facilitate construction of the 117-H Building. The depth of the soil removed was not well documented and it is not known if contamination in the soil column was adequately removed. The crib was considered a significant source of sodium dichromate.

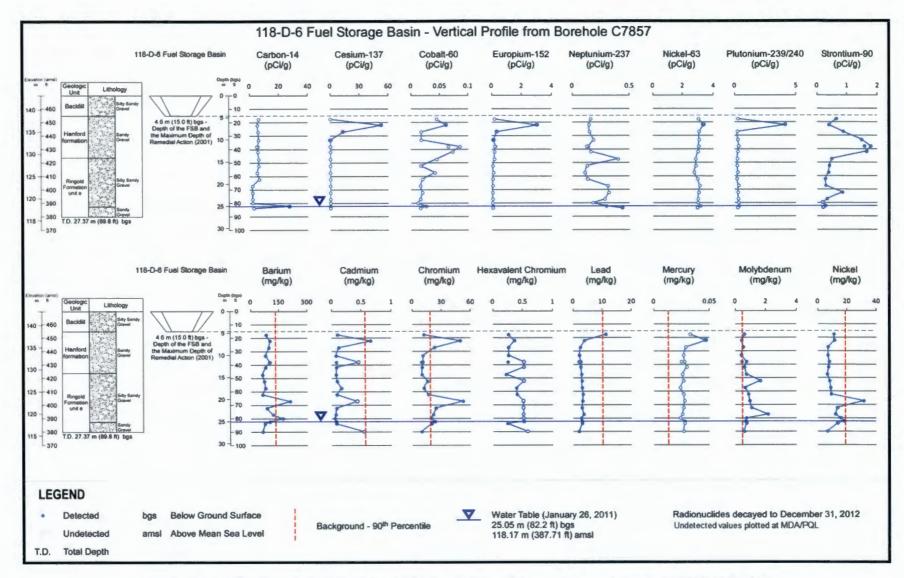


Figure 4-34. 118-D-6 Vertical Profiles of Contamination in Remedial Investigation Borehole C7857 (199-D5-142)

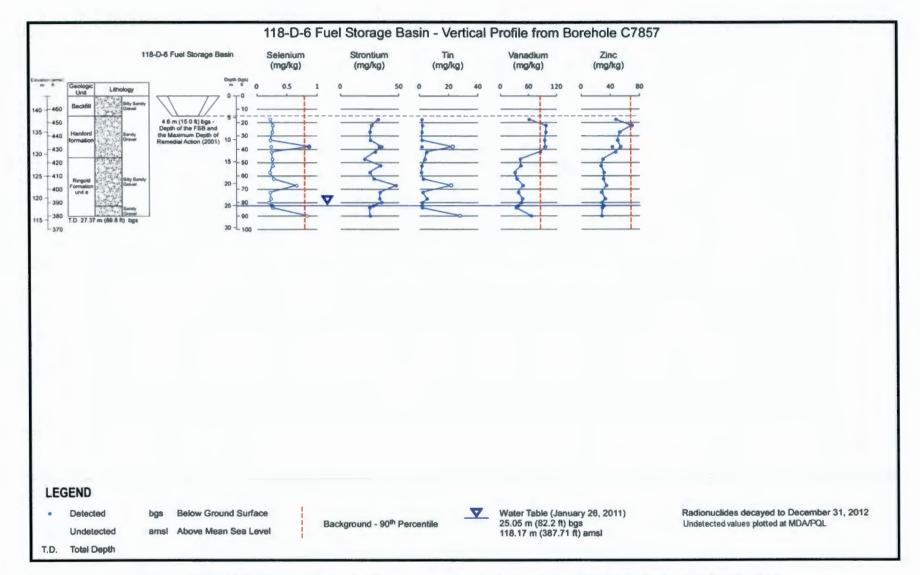


Figure 4-35. 118-D-6 Vertical Profiles of Contamination in Remedial Investigation Borehole C7857 (199-D5-142)

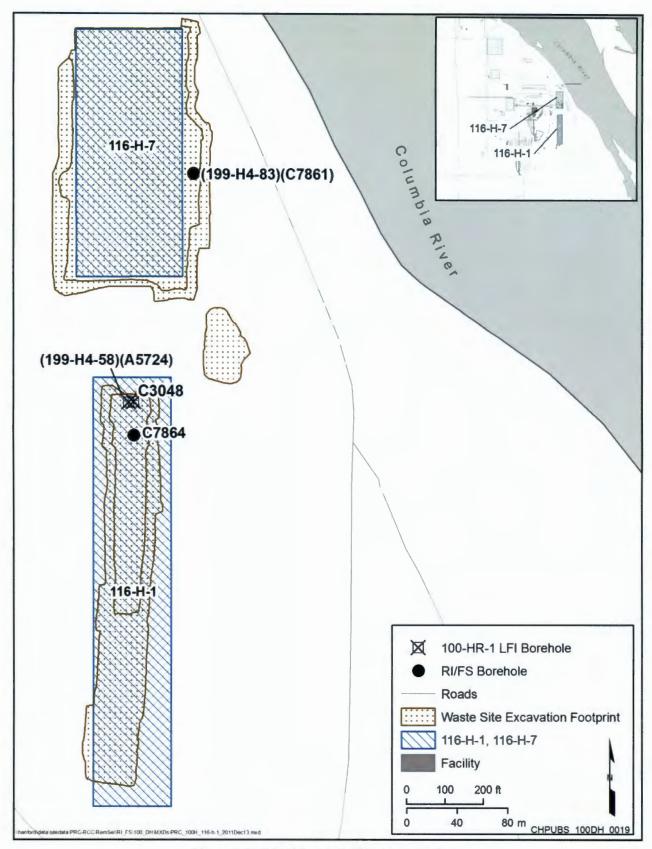


Figure 4-36. 116-H-1 and 116-H-7 Location Map

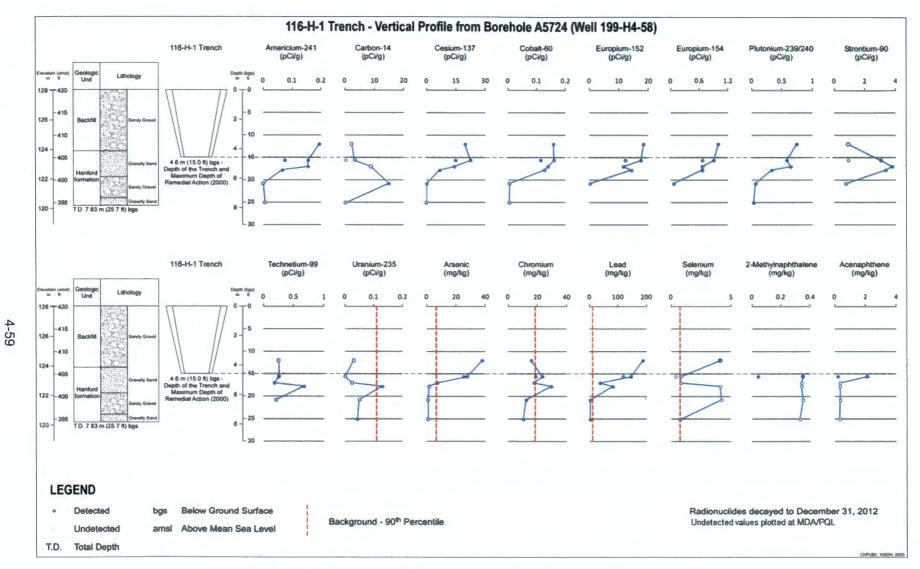


Figure 4-37. 116-H-1 Vertical Profiles of Contamination in LFI Borehole A5724 (Well 199-H4-58)

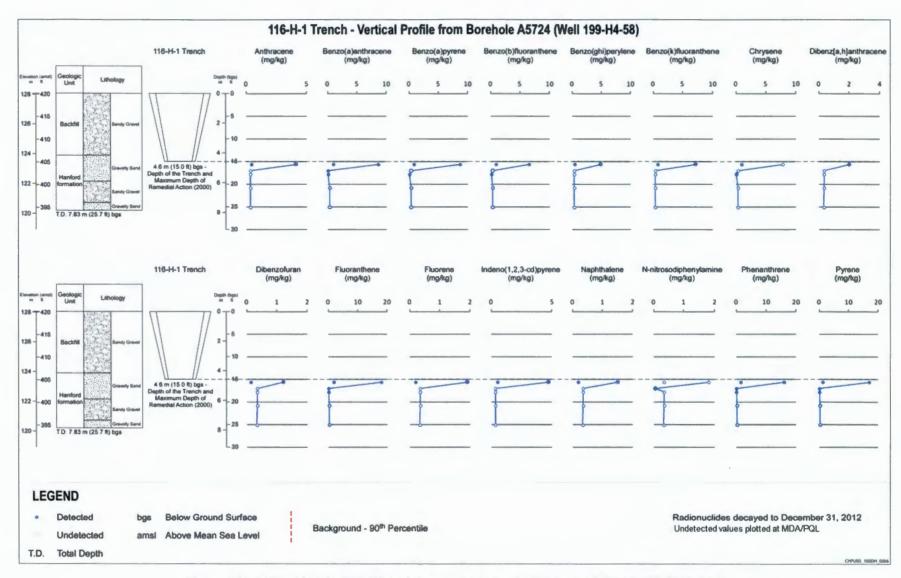


Figure 4-38. 116-H-1 Vertical Profiles of Contamination in LFI Borehole A5724 (Well 199-H4-58)

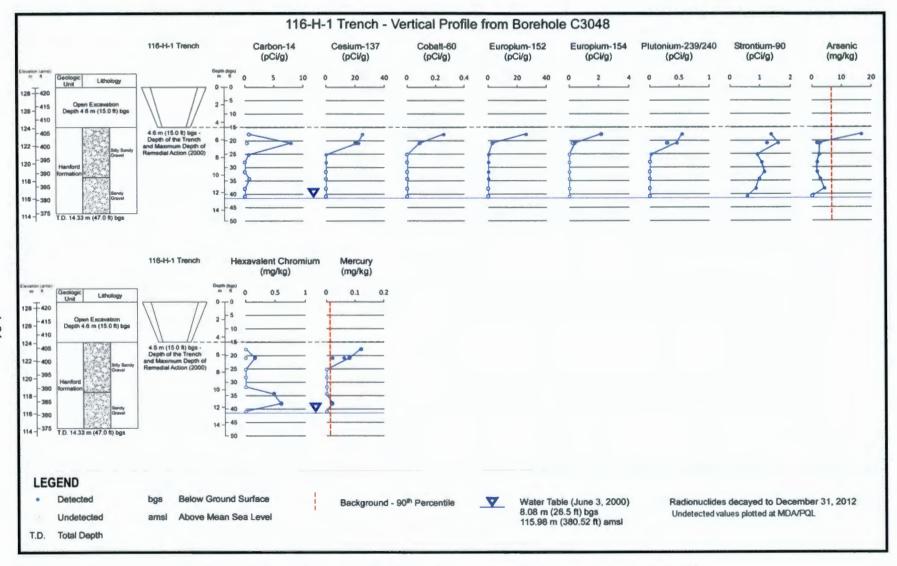
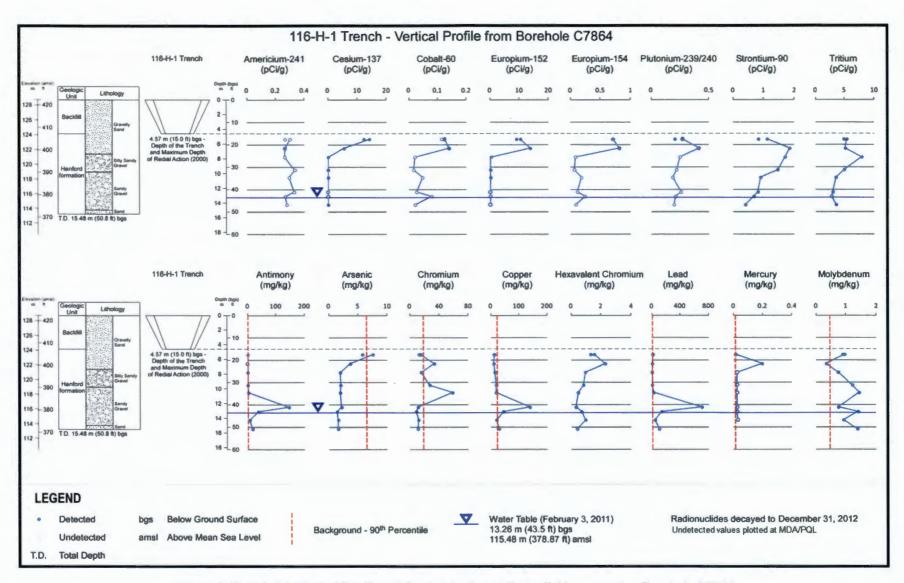


Figure 4-39. 116-H-1 Vertical Profiles of Contamination in Excavation Borehole C3048



4-62

Figure 4-40. 116-H-1 Vertical Profiles of Contamination in Remedial Investigation Borehole C7864

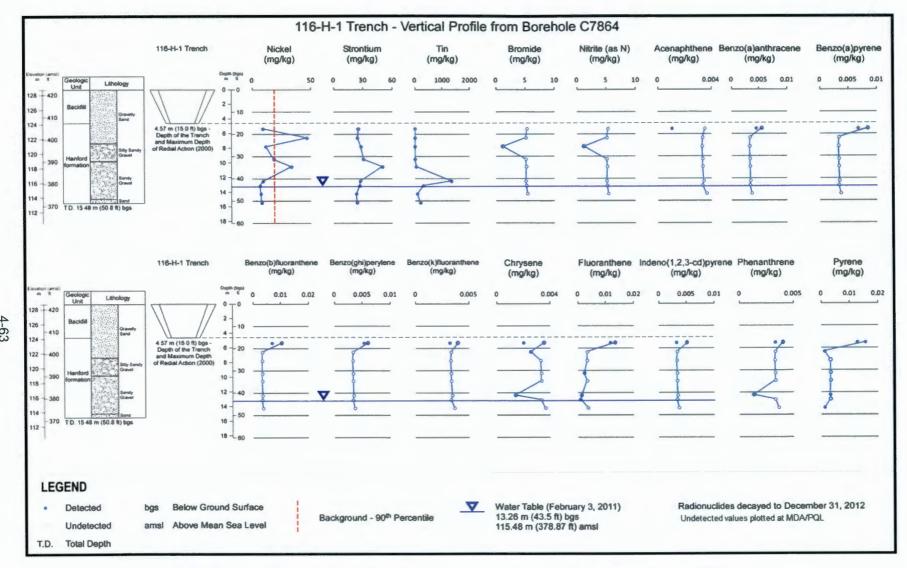


Figure 4-41. 116-H-1 Vertical Profiles of Contamination in Remedial Investigation Borehole C7864



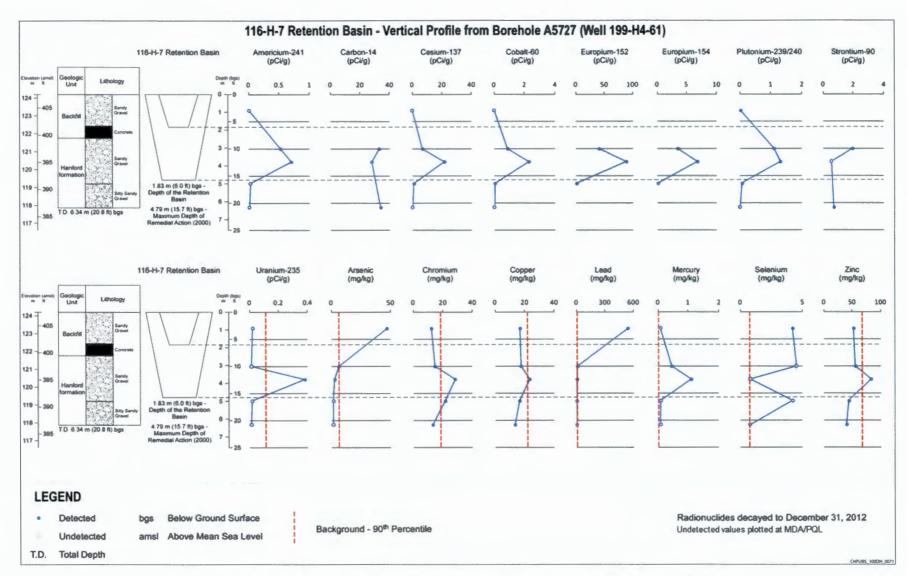


Figure 4-42. 116-H-7 Vertical Profiles of Contamination in LFI Borehole A5727 (Well 199-H4-61)

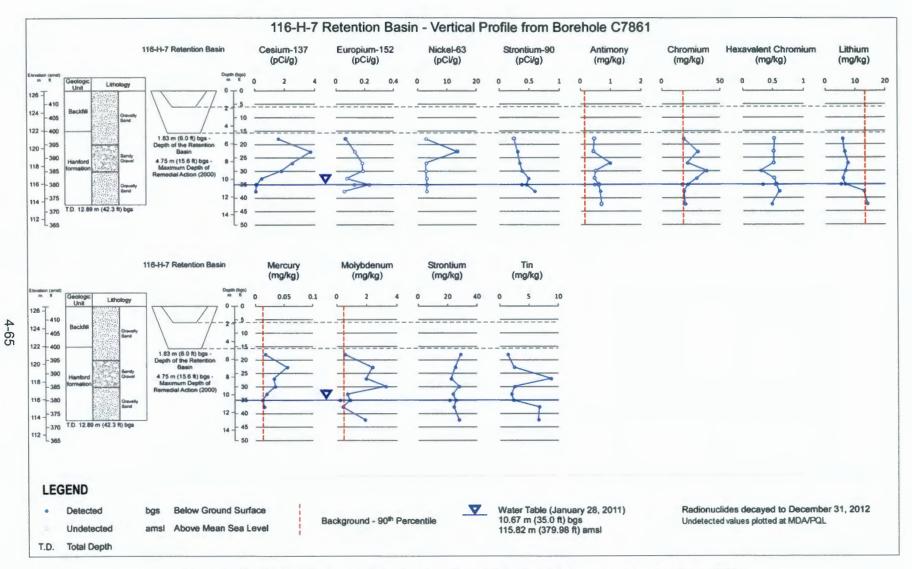


Figure 4-43. 116-H-7 Vertical Profiles of Contamination in Remedial Investigation Borehole C7861

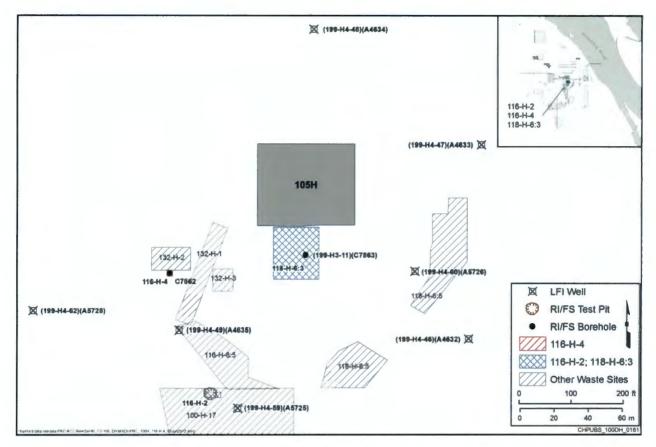


Figure 4-44. 116-H-2, 116-H-4, and 118-H-6:3 Location Map

An RI borehole (C7862) was drilled through the crib (Figure 4-44) and soil samples were collected and analyzed to evaluate the vertical extent of analytes in the vadose zone from a depth of 1.46 m (4.8 ft) bgs to the water table (13.7 m [44.8 ft]) bgs. No other soil data are available from this site. Summary data for the RI borehole are presented in Appendix D (Table D-90). Figure 4-47 presents vertical profiles of borehole contamination detected for contaminants without background values or present above background.

The RI results for the crib indicate that nine contaminants were detected or were present in the vadose zone above background concentrations. Contaminant concentrations generally decrease with depth, although carbon-14 and tritium had higher concentrations at about 40 ft bgs. Only Cr(VI) was detected in groundwater wells near the 116-H-4 crib in excess of drinking water standards (see Figure 4-3). Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The RI data are also used in Chapter 6 for the human health risk evaluation.

### 4.3.16 118-H-6 Reactor Fuel Storage Basin Characterization

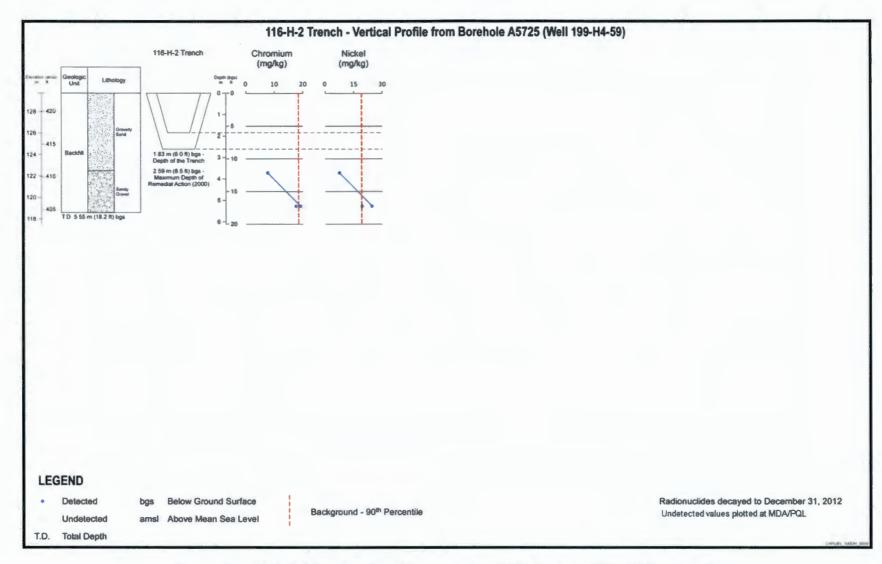
The 118-H-6 Reactor FSB was used to store irradiated fuel elements from 1949 to 1965. The basin leaked during operations and contamination extended beyond the depth of remedial excavation (7.5 m [26.5 ft]). The FSB was also identified as a site that should be characterized to determine if leaked contamination from it might now be located under the 105-H ISS reactor structure.

An RI borehole C7863 (Well 199-H-3-11, Figure 4-44) was drilled and sampled to evaluate the vertical extent of contamination through the vadose zone to the water table (14.6 m [48 ft] bgs). Summary data for

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the CVP and RI borehole are presented in Appendix D (Table D-97). Vertical profiles of borehole contamination detected or present above background are in Figure 4-48.

The CVP and RI analytical results for the FSB indicate that 21 contaminants were detected or present above background in the vadose zone. Contaminant trends generally decrease with depth at this site. However, strontium-90, total chromium, mercury, molybdenum, and tin concentrations are greater toward the water table. Only Cr(VI) is detected in nearby groundwater wells in excess of DWSs (see Figure 4-3). The absence or low concentration of Cr(VI), total chromium, and strontium-90 in the RI borehole results suggest that the vadose zone beneath the FSB is not contributing to local groundwater quality and historical FSB leaks are not likely under the ISS 105-H Reactor. Chapter 5 compares soil concentrations detected or present above background to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL). The RI data are also used in Chapter 6 for the human health risk evaluation.



4-68

Figure 4-45. 116-H-2 Vertical Profiles of Contamination in LFI Borehole A5725 (Well 199-H4-59)

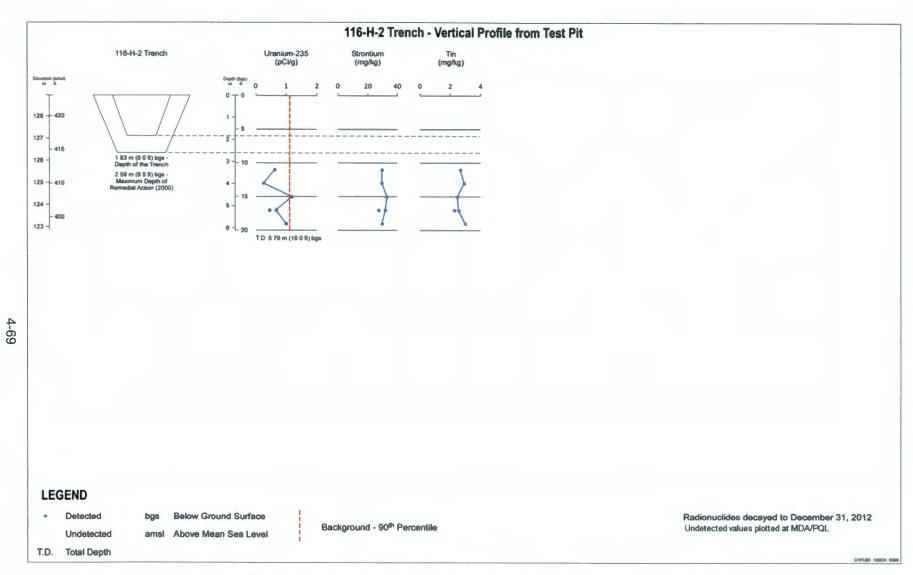


Figure 4-46. 116-H-2 Vertical Profiles of Contamination in Remedial Investigation Test Pit

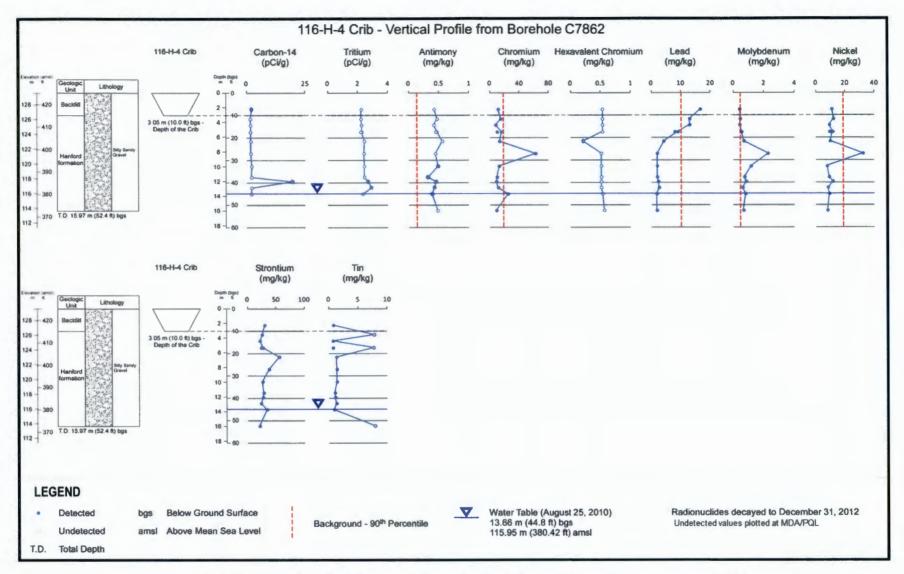


Figure 4-47. 116-H-4 Crib Vertical Profiles of Contamination in Remedial Investigation Borehole C7862

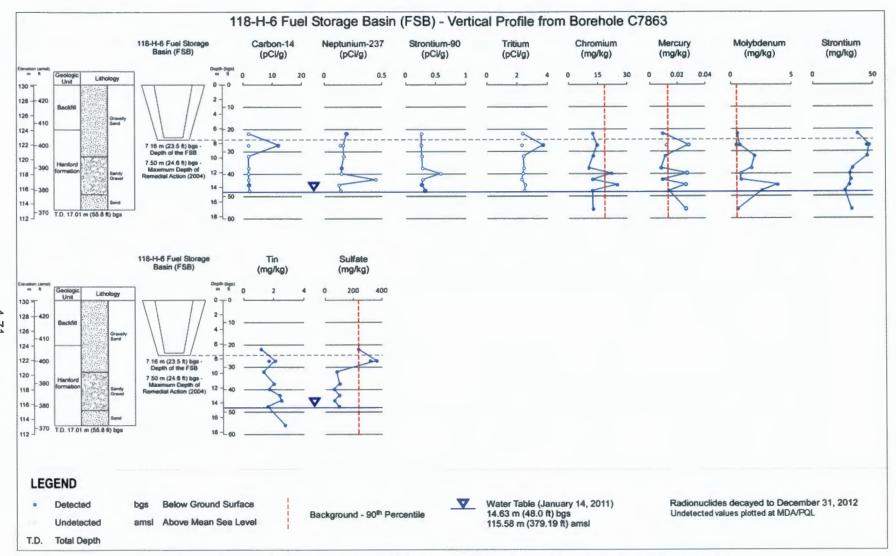


Figure 4-48. 118-H-6 Vertical Profiles of Contamination in Remedial Investigation Borehole C7863

# 4.3.17 116-H-6 and 100-H-33 Solar Evaporation Basins

The 116-H-6 and 100-H-33 waste site designations address the contaminated soil associated with the 183-H solar evaporation basins. Historically, 116-H-6 pertains to the chemical contamination beneath the site, which has been "closed-out" under RCRA ("Closure Certification for the 183-H Solar Evaporation Basins (T-1-4)" [96-EAP-246]), while 100-H-33 addresses radiological contamination. In this subsection, discussion of 116-H-6 is synonymous with 100-H-33, unless otherwise noted. The waste site and borehole/sample locations are shown in Figure 4-49.

The 116-H-6 Solar Evaporation Basin site is a RCRA TSD unit that consists of four basins. The facility was used from 1949 to 1985 to evaporate various liquid waste streams, including neutralized, spent acid etch solutions containing technetium-99 and uranium from 1973 to 1985. The basins were demolished in 1995 and 0.6 m (2 ft) of soil was removed from beneath the site. This soil removal action was based on 1991 soil data from eight boreholes (A5716 through A5723) sampled within and adjacent to the site boundary. Analytical data from the boreholes showed high levels of contamination up to 0.6 m (2 ft) below the bottom of the basin (this equated to a remediation depth of about 2.7 m (9 ft) bgs).

However, below Basin 1, soil removal continued to 4.6 m (15 ft) below the former structure (183-H Solar Evaporation Basins Postclosure Plan [DOE/RL-97-48]), indicating excavation to about 6.1 m (20 ft) bgs. A test pit was then dug below the Basin 1 excavation to 7.6 m (25 ft) bgs (183-H Solar Evaporation Basins Postclosure Plan [DOE/RL-97-48]). These test pit samples indicated nitrate and fluoride soil contamination above industrial standards (1996 MTCA Method B [WAC 173-340] and Method C 183-H Solar Evaporation Basins Postclosure Plan [DOE/RL-97-48]). Due to these results, the test pit soil from Basin 1 was disposed at the ERDF, and the site was backfilled. Protection of groundwater was demonstrated through modeling and a modified RCRA closure for 116-H-6 that included groundwater monitoring ("Closure Certification for the 183-H Solar Evaporation Basins (T-1-4)" [96-EAP-246]).

During the RI, an additional borehole, C7860 (Well 199-H4-84) associated with Basin 1 was drilled and sampled within the site boundary to the water table 12.6 m (41.5 ft) bgs. Summary data for the boreholes are presented in Appendix D (Tables D-93, D-92, and D-93). Vertical profiles of borehole contamination detected for contaminants without background values or present above background are presented in Figures 4-50 through 4-58.

An evaluation of the borehole and test pit sample results for the Solar Evaporation Basin site indicates that 24 contaminants were detected or were present in the vadose zone above background concentrations within the site boundary. Contaminant trends in individual boreholes indicate that technetium-99, strontium-90, and tritium concentrations increase with depth, but their levels are typically <2 to 7 pCi/g. Nitrate reaches a maximum of 304 mg/kg at 10.2 m (33.4 ft) bgs, while Cr(VI) concentrations are <2 mg/kg beneath the site. Only eight contaminants (cobalt-60, technetium-99, antimony, cadmium, lead, selenium, nitrate, and fluoride) were detected or were present above background levels from boreholes adjacent to the site. Detecting fewer contaminants adjacent to the site suggests that transport is mainly vertical beneath the site with little lateral spreading. Cr(VI) and nitrate are the only contaminants detected above the drinking water standards beneath this site. Historically, technetium-99 and uranium have also been identified in groundwater downgradient of 116-H-6, with decreasing trends (Section 4.5.5 and 4.5.6) Contamination sources associated with the 183-H Solar Evaporation Basins are discussed further in Section 4.9.4.3. Observed concentrations in groundwater likely reflect impact from 116-H-6 during operations. Soil concentrations detected or present above background are compared to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL) in Chapter 5. The RI data are also used in Chapter 6 for the human health risk evaluation.

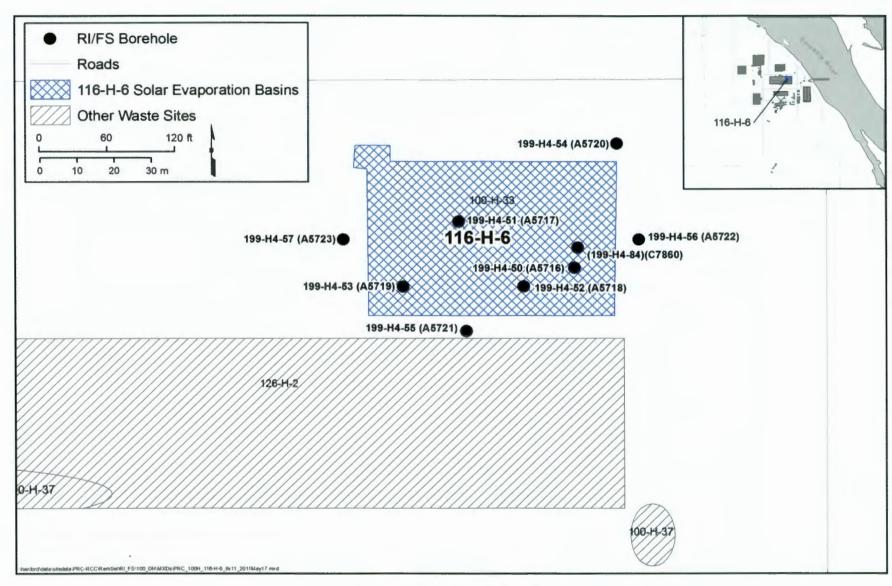


Figure 4-49. 116-H-6 Location Map

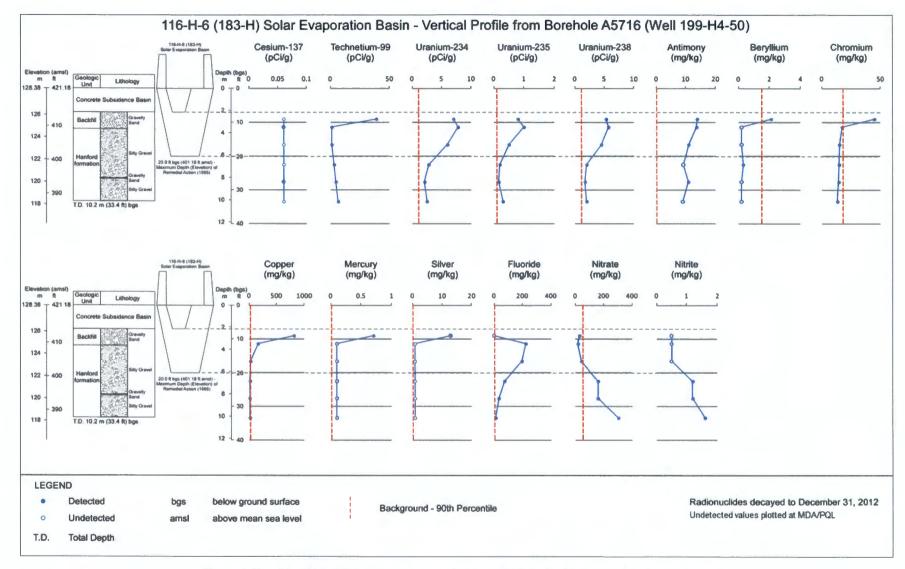


Figure 4-50. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5716 (Well 199-H4-50)

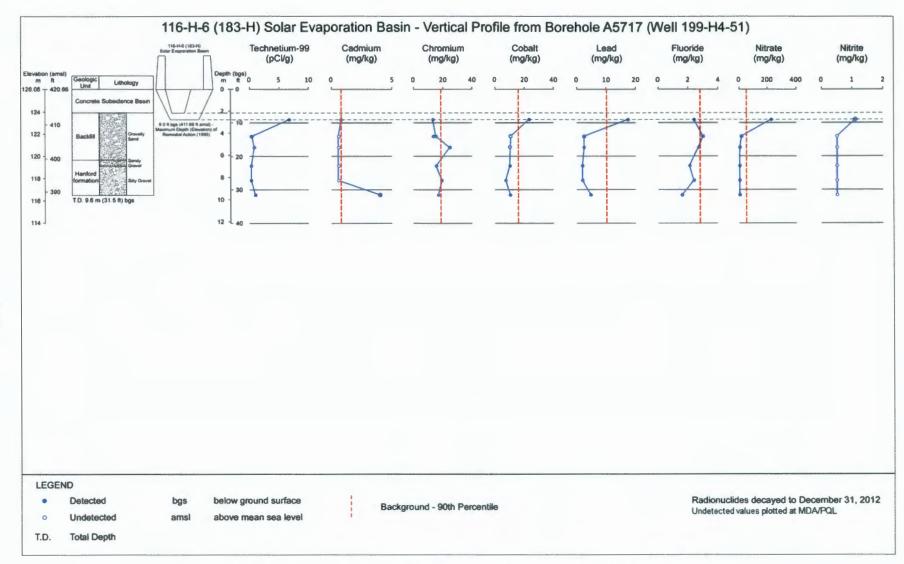


Figure 4-51. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5717 (Well 199-H4-51)

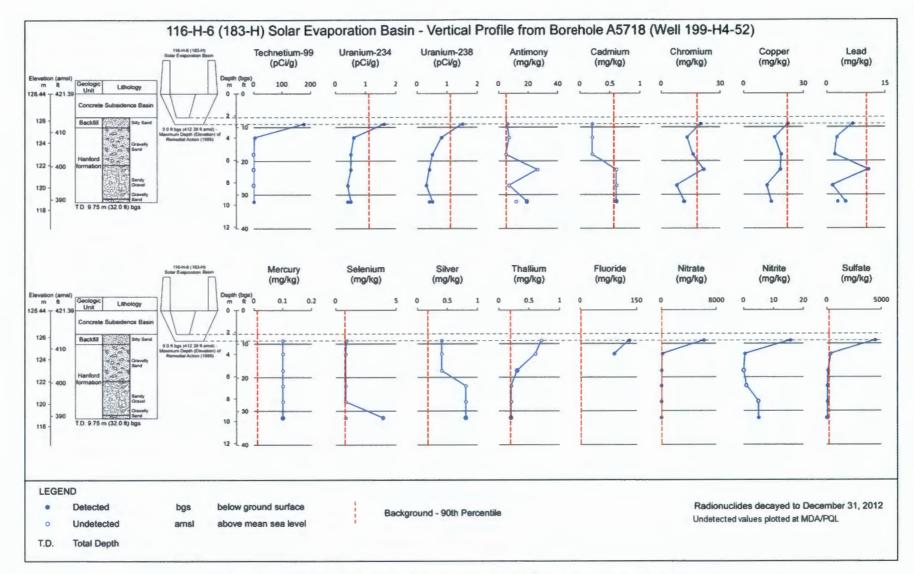


Figure 4-52. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5718 (Well 199-H4-52)

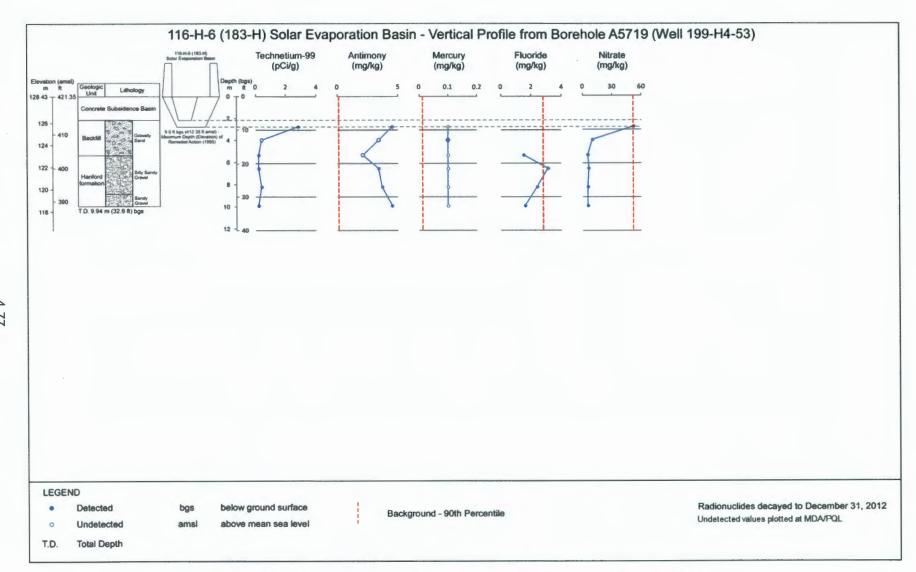


Figure 4-53. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5719 (Well 199-H4-53)

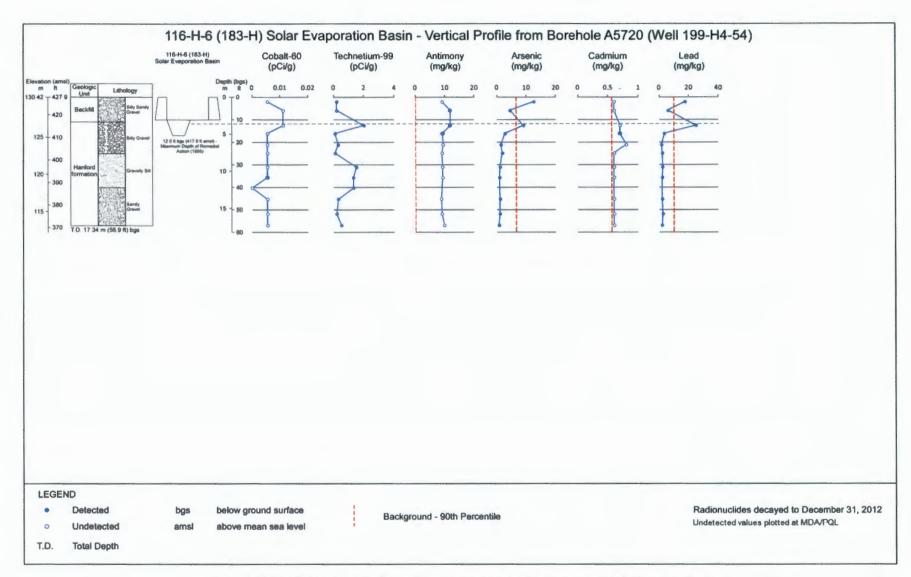


Figure 4-54. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5720 (Well 199-H4-54)

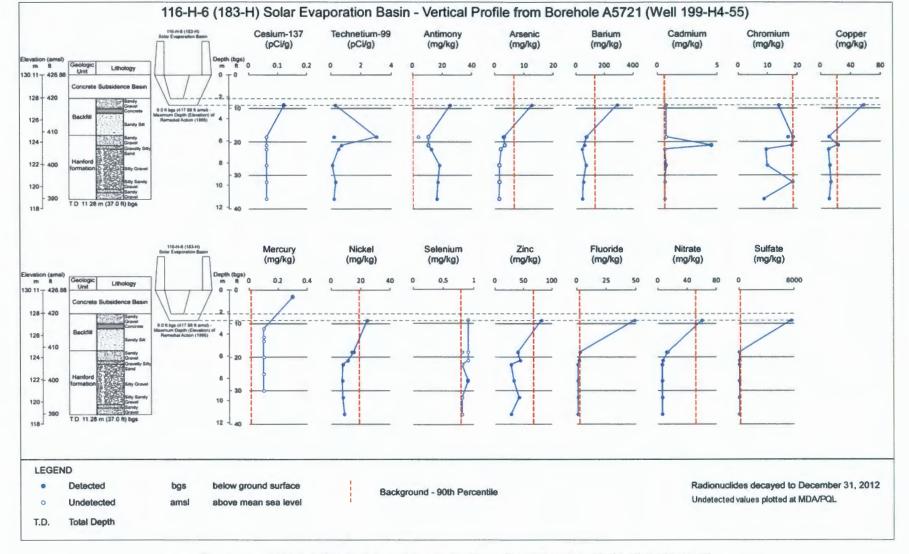


Figure 4-55. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5721 (Well 199-H4-55)

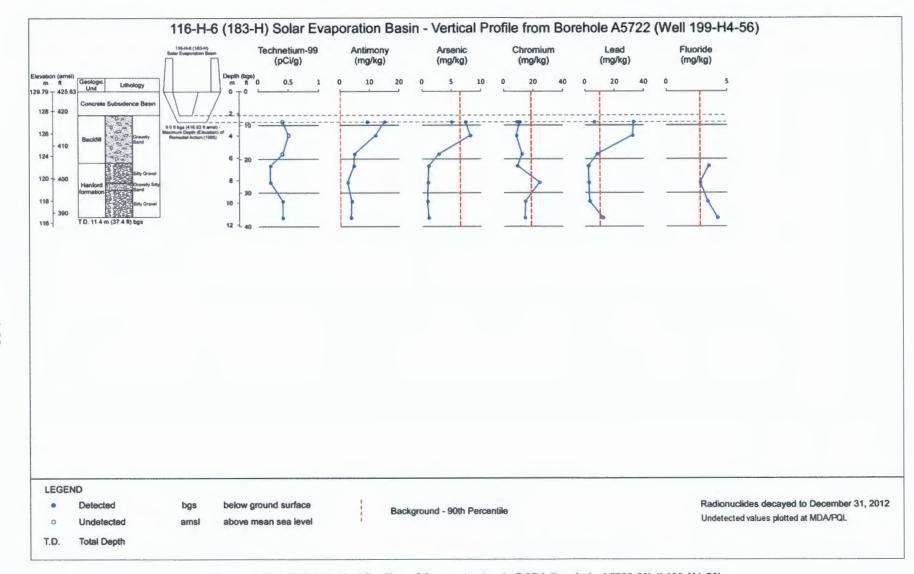


Figure 4-56. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5722 (Well 199-H4-56)

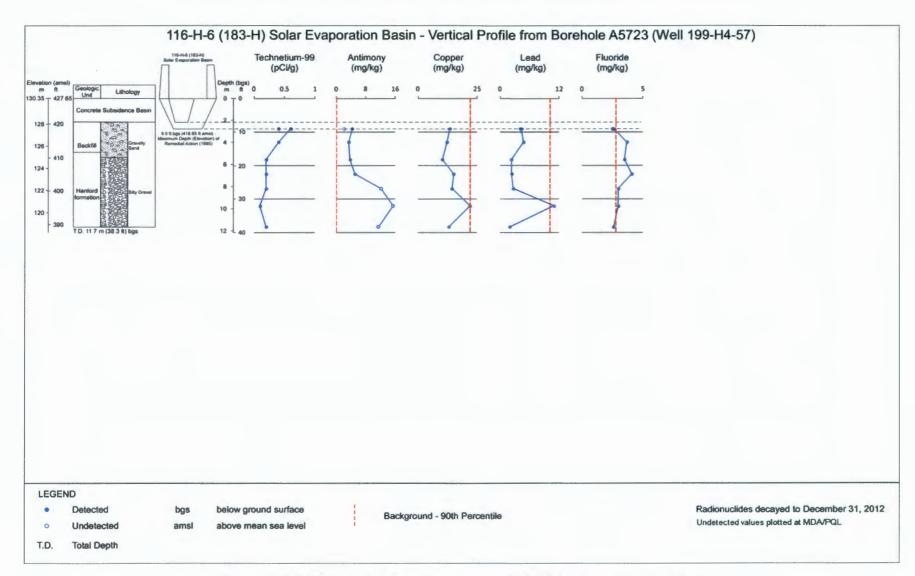


Figure 4-57. 116-H-6 Vertical Profiles of Contamination in RCRA Borehole A5723 (199-H4-57)

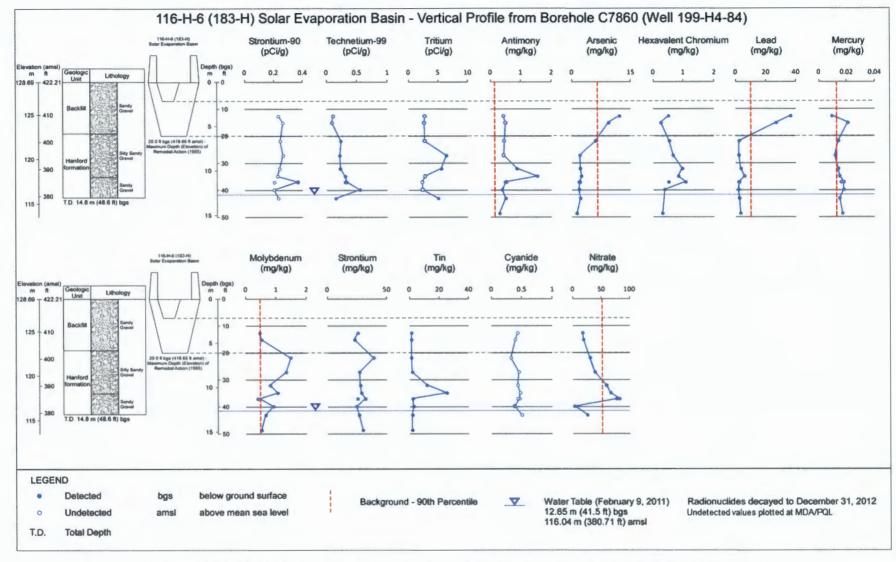


Figure 4-58. 116-H-6 Vertical Profiles of Contamination in Remedial Investigation Borehole C7860 (Well 199-H4-84)

### 4.3.18 1607-H4 Septic System Characterization

The 1607-H4 Septic System received sanitary sewage from the 181-H Pump House from 1948 to 1965. During interim remedial action, the site was excavated to 3.6 m (11.8 ft) bgs and elevated metal and PAH concentrations were detected in tank sludge and CVP samples collected during cleanup verification. In addition, the site is located in an area with a relatively shallow water table (8.8 m [28.9 ft] bgs).

An RI test pit was excavated through the trench location (Figure 4-59) and soil samples were collected and analyzed to evaluate the vertical extent of contamination to a depth of 5.6 m (19 ft). The CVP and RI data are summarized in Appendix D (Table D-98). The RI borehole data for contaminants detected or present above background levels are presented in Figure 4-60 and 4-61.

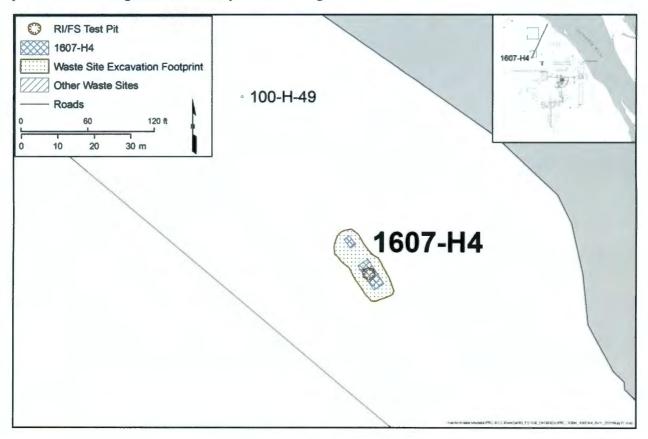


Figure 4-59. 1607-H4 Location Map

Between the CVP and RI sample results for this trench, 21 contaminants, including 15 polycyclic aromatic hydrocarbons (PAH), were detected or were present above background in the vadose zone. Contaminant concentrations decrease with depth, with the exception of lead. Lead concentrations increase with depth to 5.8 m (19 ft). None of the contaminants detected in the 1607-H4 test pit are present in downgradient groundwater wells in excess of drinking water standards (see Figure 4-3). Chapter 5 compares soil concentrations detected or present above background to soil concentrations protective of groundwater and surface water (i.e., PRG, SSL). The RI data are also used in Chapter 6 for the human health risk evaluation.

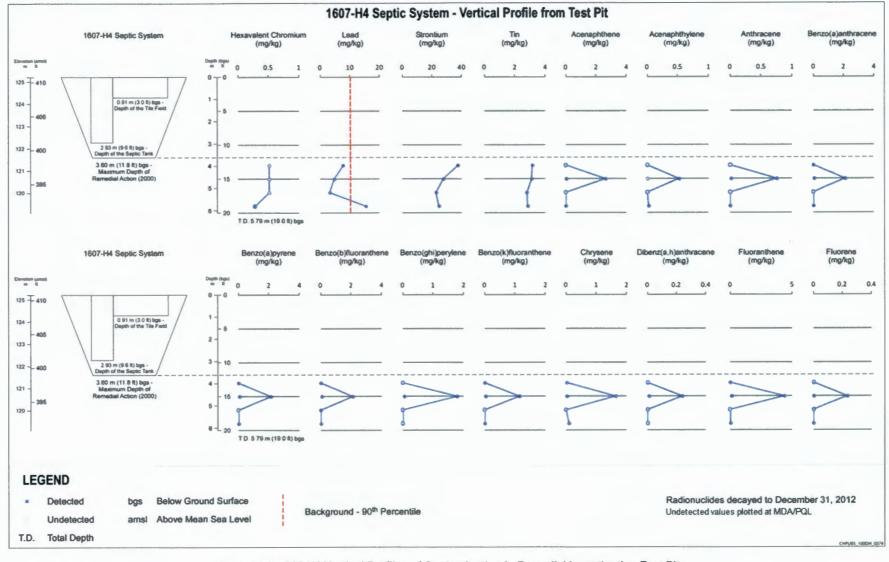


Figure 4-60. 1607-H4 Vertical Profiles of Contamination in Remedial Investigation Test Pit

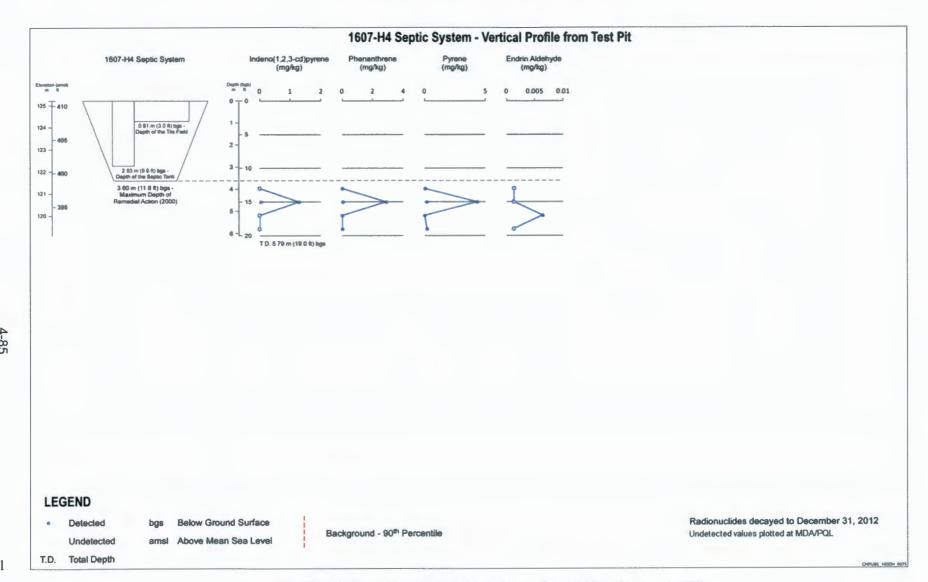


Figure 4-61. 1607-H4 Vertical Profiles of Contamination in Remedial Investigation Test Pit

### 4.3.19 New RI Well Soil and Sediment Sampling

This summary describes the nature and extent of vadose zone contamination above background and aquifer sediment and groundwater concentrations for the wells identified in Table 4-4. The well locations are shown in Figures 2-1 and 2-2.

Table 4-4. Identification of 100-D/H RI Wells with Vadose Zone and Aguifer Sediment Samples

Well Identification	Borehole Identification	RI Area, 100-D/H SAP (DOE/RL-2009-40) Well ID*		
199-D3-5	C7620	100-D, Well 2		
199-D5-133	C7621	100-D, Well 3		
199-D5-132	C7622**	100-D, Well 4		
199-D6-3	C7623	100-D, Well 5		
199-D5-140	C7866**	100-D, Well 9		
199-D5-143	C8375**	100-D, Replacement Well 9		
199-D5-134	C7624	100-D, Well R4		
199-D5-141	C7625**	100-D, Well R5		
199-D5-144	C8668**	100-D, Replacement Well R5		
199-Н3-6	C7626	100-H, Well 6		
199-Н3-7	C7627	100-H, Well 7		
199-Н6-3	C7628	100-H, Well 10		
199-Н6-4	C7629	100-H, Well 11		
199-H1-7	C7630	100-H, Well 12		
199-Н3-9	C7639	100-H, Well R1		
199-Н3-10	C7640	100-H, Well R2		
199-H2-1	C7631	100-H, Well R3		

Source: Sampling and Analysis Plan for the 100-DR-1, 100-DR-2, 100-HR-1, 100-HR-2, and 100-HR-3 Operable Units Remedial Investigation/Feasibility Study (DOE/RL-2009-40).

#### 4.3.19.1 Vadose Zone Soil and Aquifer Sediment Samples

Vadose zone soil and aquifer sediments were collected for each well within 1.5 m to 4.6 m (5 to 15 ft) of the water table to characterize contaminants associated with the groundwater-vadose zone interface. Groundwater grab samples were also collected from these locations. These data are used to describe contamination associated with the PRZ. Appendix D, Tables D-73 through D-76 and Tables D-99 through D-112 summarize the soil and aquifer sediment data. Vertical profile data of wells 199-D5-132 (C7622), 199-D5-140 (C7866), 199-D5-141 (C7625), 199-D5-143 (C8375), and 199-D5-144 (C8668) are described in Sections 4.3.6, 4.3.7, and 4.3.8.

<sup>\*</sup> Wells for 100-D and 100-H RI are identified and described in *Integrated 100 Area Remedial Investigation/Feasibility Study Work Plan Addendum 2: 100-KR-1, 100-KR-2, and 100-KR-4 Operable Units* (DOE/RL-2008-46-ADD2).

<sup>\*\*</sup> Profiles and data are described in Sections 4.3.6, 4.3.7, and 4.3.8.

With few exceptions, the radionuclides analyzed were not detected in soil samples from the 12 wells discussed in this section. Low-levels of radioactive contamination were detected in soil samples from 6 of the 12 wells. The maximum concentrations for cesium-137 (C7623), strontium-90 (C7624, C7626, and C7639), and tritium (C7626, C7627, and C7630) were 0.241 pCi/g, 0.906 pCi/g, and 18.6 pCi/g, respectively. Vertical profiles of borehole radiological contamination detected in these wells are presented in Appendix D, Figures D-3 through D-6, D-9, and D-10.

The results for nonradioactive contaminants detected or present above background concentrations in the new RI wells are summarized as follows:

- Boreholes C7624, C7625, C7626, and C7628 showed elevated total chromium, nickel, and molybdenum concentrations. Concentrations of total chromium and nickel were highest in C7628 at 2,900 and 1,390 mg/kg, respectively (see Appendix D, Figure D-7). Elevated concentrations of copper and cobalt were also present in the samples with the most elevated total chromium results.
- Hexavalent chromium was detected above and below the water table in boreholes C7620, C7621, C7623, C7624, C7626, C7628, C7629, C7640, and C7631. The maximum Cr(VI) concentration was 1.17 mg/kg in C7629.
- Barium was reported in one or more samples from C7623 and C7624 at a maximum concentration of 192 mg/kg.
- Thallium was detected in C7627 and C7630 at a maximum concentration of 0.278 mg/kg.
- A single detection of uranium (9.73 mg/kg) was reported just above the water table in C7626.
- Low-level detections of 2-hexanone and styrene were present in boreholes C7627 and C7629.
- Concentrations of strontium (metal) and tin were consistent with the results from other 100-D/H RI borehole samples.

With some exceptions, the radionuclide and non-radionuclide detections in the groundwater sediment samples collected from 1.5 m (5 ft) into the unconfined aquifer were similar to those found in the vadose zone soils. Visually, these exceptions can be observed in the profiles presented in Appendix D (Figures D-1 to D-12).

### 4.3.19.2 RUM Material Soil Samples

Soil samples were collected from the RUM material in RI wells that extended to the RUM surface or deeper. These samples represent the aquitard, and are from the material separating the unconfined aquifer and the first water bearing unit of the RUM. Soil samples were also collected from lower aquifers in wells that were completed in the first water bearing unit of the RUM. Table 4-5, presents the hexavalent chromium results from those samples. Appendix D includes all of the soil sampling analytical results.

Carlo		Sample Depth Range (ft bgs)		AND REPORT OF THE PARTY OF THE	RUM Depth (ft bgs)		
Well ID	Cr(VI) Result (mg/kg)		Тор	Bottom	Top	Bottom <sup>a</sup>	Sample Location
199-D3-5	0.571	U	104.99	105.10	104	Unknown	RUM near surface
	0.0444	U	104.99	105.10	104	Unknown	RUM near surface

Table 4-5. Cr(VI) Results for Soil Samples Collected within or near the RUM

Table 4-5. Cr(VI) Results for Soil Samples Collected within or near the RUM

	CrOZD D	ocult.		epth Range bgs)		M Depth t bgs)		
Well ID	Cr(VI) Result (mg/kg)		Тор	Bottom	Тор	Bottom <sup>a</sup>	Sample Location	
	0.092	U	102.99	105.10	104	Unknown	RUM near surface	
199-D5-132	0.559	U	103.20	104.99	105	Unknown	Above RUM surface	
	0.044	U	103.20	104.99	105	Unknown	Above RUM surface	
	0.114	BN	103.20	104.99	105	Unknown	Above RUM surface	
199-D5-133	0.594	U	102.50	104.99	105.5	Unknown	Above RUM surface	
	0.0405	U	102.50	104.99	105.5	Unknown	Above RUM surface	
	0.585	U	102.50	104.99	105.5	Unknown	Above RUM surface	
	0.0626	U	102.50	104.99	105.5	Unknown	Above RUM surface	
	0.13	U	102.50	104.99	105.5	Unknown	Above RUM surface	
199-D5-134	0.12	UN	107.30	109.80	108.5	131.5	RUM near surface	
	0.609	U	107.30	109.80	108.5	131.5	RUM near surface	
	0.0462		107.30	109.80	108.5	131.5	RUM near surface	
	0.11	UN	110.99	113.50	108.5	131.5	RUM	
	0.13	U	179.00	181.50	158	190	2 <sup>nd</sup> RUM aquifer	
199-D5-140	0.282	BN	100.8 <sup>b</sup>	103.30	108	Unknown	Above RUM surface	
199-D5-141	0.12	U	137.50	139.99	135	160.5	RUM silt (transitional contact at 112.5 ft)	
199-D5-143	0.605	U	105.20	107.70	105.5	Unknown	RUM near surface	
	0.0442	U	105.20	107.70	105.5	Unknown	RUM near surface	
	0.036	U	105.20	107.70	105.5	Unknown	RUM near surface	
199-D5-144	0.155	U	103.80	106.30	108.5	Unknown	Above RUM surface	
199-D6-3	0.13	U	101.5 <sup>b</sup>	104.00	101.6	Unknown	RUM near surface	
	0.637	U	101.5 <sup>b</sup>	104.00	101.6	Unknown	RUM near surface	
	0.0358	U	101.5 <sup>b</sup>	104.00	101.6	Unknown	RUM near surface	
199-H1-7	0.14	BN	32.00	34.51	31.5	Unknown	RUM near surface	

Table 4-5. Cr(VI) Results for Soil Samples Collected within or near the RUM

	Cr(VI) Result			epth Range bgs)		M Depth it bgs)	
Well ID	(mg/k		Тор	Bottom	Тор	Bottoma	Sample Location
	0.61	U	32.00	34.51	31.5	Unknown	RUM near surface
	0.0389	U	32.00	34.51	31.5	Unknown	RUM near surface
	0.53	U	29.80	32.30	31.5	Unknown	Above RUM surface
	0.53	U	29.80	32.30	31.5	Unknown	Above RUM surface
	0.53	U	29.80	32.30	31.5	Unknown	Above RUM surface
	0.53	U	29.80	32.30	31.5	Unknown	Above RUM surface
	0.55	U	29.80	32.30	31.5	Unknown	Above RUM surface
199-H2-1	0.128	В	37.80	40.29	37	59	RUM near surface
	0.13	U	99.02	101.50	97	105	RUM below 1 <sup>st</sup> aquifer, transitional
	0.14	U	119.00	121.10	105	121	RUM silt
199-H3-10	0.13	U	55.71	58.20	55	71	RUM near surface, transitional
	0.13	U	80.18	82.71	76	97	RUM
	0.12	U	118.70	120.90	114	197	RUM below 1 <sup>st</sup> aquifer
199-Н3-6	0.14	UN	54.89	56.89	54.5	Unknown	RUM near surface
	0.662	U	54.89	56.89	54.5	Unknown	RUM near surface
	0.0343	U	54.89	56.89	54.5	Unknown	RUM near surface
199-Н3-7	0.672	U	51.11 <sup>b</sup>	53.61	52.5	Unknown	RUM near surface
	0.0329	U	51.11 <sup>b</sup>	53.61	52.5	Unknown	RUM near surface
	0.13	UN	51.11 <sup>b</sup>	53.61	52.5	Unknown	RUM near surface
199-Н3-9	0.12	UN	50.98	53.51	50	70.5	RUM near surface
	0.12	UN	75.20	77.20	74	76	RUM above 1 <sup>st</sup> aquifer
	0.12	UN	100.00	102.00	97	171	RUM below 1 <sup>st</sup> aquifer
199-Н6-3	0.13	UN	60.50	62.99	60	Unknown	RUM
	0.633	U	60.50	62.99	60	Unknown	RUM
	0.0367	U	60.50	62.99	60	Unknown	RUM

Table 4-5. Cr(VI) Results for Soil Samples Collected within or near the RUM

Well ID Cr(VI) Result (mg/kg)		The second second second second	Sample Depth Range (ft bgs)		M Depth it bgs)		
			Top	Bottom	Top	Bottom <sup>a</sup>	Sample Location
199-H6-4	0.652	U	56.29 <sup>b</sup>	58.79	57	Unknown	RUM near surface
	0.0348	U	56.29 <sup>b</sup>	58.79	57	Unknown	RUM near surface
	0.12	U	56.29 <sup>b</sup>	58.79	57	Unknown	RUM near surface

a. "Unknown" indicates the bottom of the unit was not encountered during drilling

bgs = below ground surface

ID = identification

RUM= Ringold Formation upper mud unit

### 4.3.20 Potentially Significant Cr(VI) Waste Sites Undergoing Active Interim Remediation

Interim remedial actions are presently being performed at several 100-D sites with known or potential Cr(VI) contamination. All these sites are associated with pre-reactor handling and use of concentrated sodium dichromate solutions and are identified in Chapter 1 on Figure 1-14. Interim remediation will continue at these sites, and is expected to be complete before issuance of a final action ROD. However, brief summaries of the current state and data for these sites, as of early November 2013, are provided to support an understanding of ongoing remediation at sites of particular potential relevance as sources of Cr(VI) contamination. Although a technical evaluation of future effect to groundwater has not been performed, one or more of these sites very strongly suggest a continuing source of aquifer contamination near the Cr(VI) groundwater plume. 100-D-100 appears to be the worst-case Cr(VI) site, based on concentrations observed in the deep vadose zone. Remediation of these sites has not been completed or was not completed prior to the quantitative site evaluations presented in following chapters. As such, these sites are considered in the feasibility study as still requiring additional remediation, but more current available data is summarized to provide context for the overall conceptual site model. Closeout verification data from these sites will be evaluated at the completion of interim remedial actions to verify protection of human health and the environment. Results from these and other accepted waste sites will be integrated into the final ROD as results are available.

100-D-73. The 100-D-73 waste site consists of the footprint of the former 108-D Building, where concentrated Cr(VI) solution was initially prepared during historical operations. Remediation of the site extended up to 5.5 m (18 ft) bgs, including removal of localized stained concrete with 3,020 mg/kg Cr(VI). No significant Cr(VI) inventory was identified during remediation, and interim remediation and reclassification of the site has been completed. Elevated Cr(VI) concentrations in soil during remediation were found only in the south-central portion of the site, with a maximum Cr(VI) concentration of 16.8 mg/kg identified at 3 m (10 ft) bgs. Total chromium concentrations in soil samples collected near this waste site are generally within typical Hanford Site background concentrations (18.5 mg/kg), with a maximum detected concentration of 19.8 mg/kg.

b. Based on a 0.76m (2.5 ft) split spoon length and the recorded sample bottom depth.

U = Analyte not detected above the method detection limit

B = Analyte was detected in the method blank and in the sample

N = Spike sample recovery is outside of control limits

100-D-30. The 100-D-30 waste site addresses residual sodium dichromate contamination in soil and concrete rubble associated with the former 185-D facility sodium dichromate trench and mixing tanks. Stained soils and concrete were observed during initial remediation, with analytical sample results for Cr(VI) up to 108 mg/kg in soil samples collected from waste material. Initial remediation extended up to 3.5 m (12 ft) bgs at the location of a former sump in the pipe trench. Further subsurface characterization in the sump area detected slightly elevated Cr(VI) and total chromium concentrations at depth (*Report on Investigation of Hexavalent Chromium Source in the Northern 100-D Area* [DOE/RL-2010-40]). Based on these detections, additional remediation has been performed in the sump area, currently extending to a depth of approximately 22.9 m (75 ft). The Ringold Formation was encountered at approximately 13.7 m (45 ft) bgs and Cr(VI) concentrations up to 140 mg/kg (at approximately 21.3 m [70 ft] bgs) have been observed. Remediation is planned to continue to an estimated elevation of 118 m AMSL (approximately 25 m [82 ft] bgs).

100-D-104. The 100-D-104 waste site addresses an area of vadose zone contamination, including Cr(VI), discovered immediately southeast of the former 185-D Building and 100-D-30 waste site. Upon discovery, contaminated soil was initially removed to a depth of approximately 6 m (20 ft). Multiple colors of soil staining were still observed at this depth, and separate analytical samples showed a range of contaminant concentrations: Cr(VI) was quantified between 0.24 and 286 mg/kg; total chromium was quantified between 2.8 mg/kg and 303 mg/kg; sulfate results ranged from undetected to 4,590 mg/kg. The disparity in the nature of the staining within a small area is suggestive of multiple historical releases. The most likely source of the contamination is a former acid neutralization French drain located at nearly the exact location of the staining, which would account for the elevated sulfate levels observed in some samples. An external sodium dichromate storage tank was also located immediately nearby and may have had releases to the drain or immediate vicinity.

Additional subsurface characterization was performed at the locations of the acid neutralization French drain and the sodium dichromate storage tank (*Report on Investigation of Hexavalent Chromium Source in the Northern 100-D Area* [DOE/RL-2010-40]). No significant Cr(VI) was detected beneath the former storage tank, with a maximum result of 0.25 mg/kg at approximately 7.5 m (25 ft) bgs. Total chromium was detected above background levels at up to 112 mg/kg at a total depth of approximately 5 m (20 ft), decreasing to 28.1 mg/kg at a depth of approximately 7.5 m (25 ft). Higher contamination levels were observed in samples collected beneath the former French drain, with results of up to 14.2 mg/kg The Ringold Formation was encountered at a depth of approximately 15.8 m (52 ft). Cr(VI) concentrations increased with depth below the Ringold contact from 78.6 mg/kg at a depth of 16.8 m (55 ft) to a maximum of 212 mg/kg at 19.8 m (65 ft) bgs. The contamination plume has been observed to be trending southeast with depth, consistent with the local dip of the surface of the Ringold Formation. The excavation is currently at a depth of approximately 21.3 m (70 ft) and is planned to continue to an estimated elevation of 118 m AMSL (approximately 25 m [82 ft] bgs).

100-D-100. The 100-D-100 waste site addresses an area of stained soil discovered adjacent to the former railroad spur servicing the 183-DR Head House. The stained area is also near the former railcar unloading station (100-D-12 waste site), but on the opposite (southern) side of the former railroad junction. Initial surficial sampling at the stained area showed up to 2,110 mg/kg of Cr(VI) present. However, at 0.3 m (1 ft) bgs, the Cr(VI) concentration decreased significantly (87 mg/kg), with a corresponding total chromium concentration of 150 mg/kg. A higher proportion of silt was observed in this sample relative to other shallow samples collected.

Initial characterization of soil at the 100-D-100 waste site extended to 4.6 m (15 ft) bgs, where the maximum Cr(VI) and total chromium detections were 17.6 mg/kg and 31 mg/kg, respectively. Sulfate concentrations above Hanford Site background (up to 920 mg/kg) were quantified in several of the

samples, suggesting that sulfuric acid may also have been released at this location. Remediation of this site has revealed significant visual staining and soil contamination with up to 709 mg/kg Cr(VI). Remediation of this site is currently at a depth of approximately 22.9 m (75 ft) bgs, where the maximum detected Cr(VI) concentration is 242 mg/kg. Remediation is planned to continue to an estimated elevation of 118 m AMSL (approximately 25 m [82 ft] bgs.

100-D-77. The 100-D-77 waste site consists of the footprint of the former 183-DR facility, used for water treatment for the 105-DR Reactor, including handling, storage, and injection of sodium dichromate. Remediation included the former head house and yard area, where sodium dichromate and sulfuric acid solutions were stored, and the sample room area, where sodium dichromate was injected into cooling water. Remediation extended to a maximum depth of 9.5 m (31 ft) bgs in the head house area, and interim remediation and reclassification of the site has been completed. No significant residual Cr(VI) inventory was identified during remediation. Cr(VI) was detected in residual structural concrete components with up to 7.7 mg/kg in a former acid trap. Stained soils have been observed, but the highest soil Cr(VI) concentration detected was 2.38 mg/kg, with a corresponding total chromium concentration of 59.7 mg/kg. Remediation was driven primarily by removal of subgrade structural components and mercury contamination in soil above interim action RAGs. Mercury was likely present because of spills of contaminated sulfuric acid. 100-H-46. The 100-H-46 waste site consisted of contaminated soils, concrete structures, and drain pipes beneath the former 190-H Main Process Pump House sodium dichromate process equipment, piping, unloading dock, and railroad spur. Remediation has extended to a maximum depth of 12.5 m (41 ft), and verification sampling is in-progress. Stained concrete was identified during remediation of residual structural components, with up to 3,830 mg/kg Cr(VI) in concrete. No substantial soil-contaminant plume was identified—the highest Cr(VI) concentration detected in soil was 10.7 mg/kg—but low concentrations slightly above interim remedial action goals drove remediation to the stated depth.

# 4.3.21 RPO Soil Sampling Summary to Support RI/FS

A total of 70 RPO wells were installed. The RPO wells are shown on Figure 4-62. Soil samples were collected from the RUM surface for the RPO process and analyzed for Cr(VI) and permeability. In addition, soil samples were collected from 9 of 70 RPO boreholes (199-D4-96, 199-D5-128, 199-D7-5, 199-D7-6, 199-D8-89, 199-H1-2, 199-H1-35, 199-H1-36, and 199-H1-4) specifically to support the RI/FS. These samples were analyzed for select radionuclides, metals, and physical properties (*Sampling and Analysis Plan for Installation of 100-HR-3 Groundwater Operable Unit Remedial Process Optimization Wells* [DOE/RL-2009-09]). Sample locations for the RI/FS included locations: two feet above the water table, within the top half of the aquifer, within the lower half of the aquifer, and from the top 2 m (5 ft) into the RUM surface. The data provide additional information for physical and hydrogeologic parameters to support possible future fate and transport evaluations, particularly beneath the unconfined aquifer.

Several metals and one radionuclide (strontium-90 as total beta radiostrontium) were detected above the 90<sup>th</sup> percentile of established background concentrations (see Table 4-1). Table 4-6 presents a summary of analytes that were detected above background levels. The detection limit for antimony is greater than the background concentration of 0.13 mg/kg. Antimony was detected in only two samples. Silver concentrations were not detected above background concentrations; however, the detection limit is slightly above background in eight samples. Boron was detected above background in all but one sample. The detections of boron are not included in Table 4-6 because they are flagged as estimated values as a result of interference. Total beta radiostrontium had a low level detection in Well 199-H1-36; however, the result was well below the minimum detectable activity, and is therefore not included in Table 4-6.

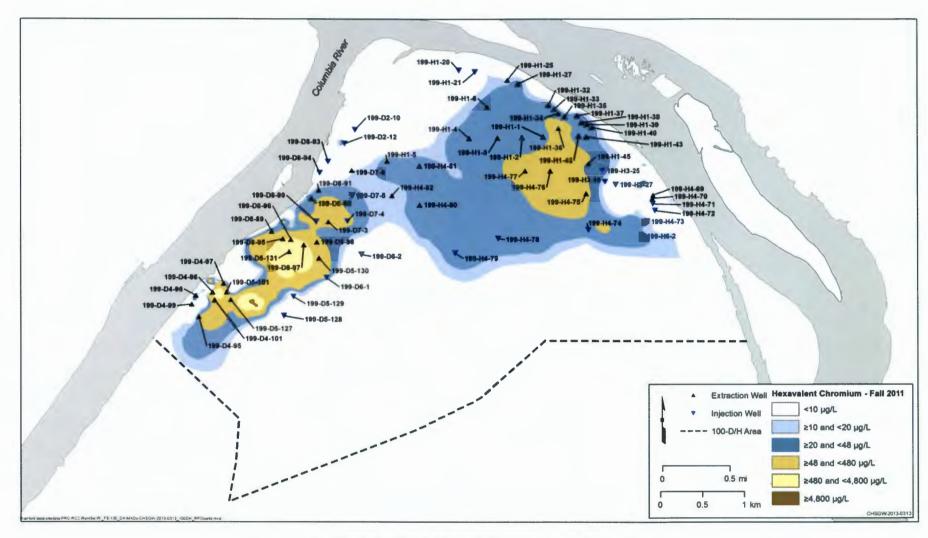


Figure 4-62. Location of Remedial Process Optimization Wells in 100-D/H

Table 4-6. Summary of Detections Above Background from Remedial Process Optimization Wells

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Well ID	Sample ID	Sample Bottom Depth (m)	Sample Bottom Depth (ft)	Analyte	Result (in mg/kg unless noted)	
199-D4-96	B22HT8	29.26	96	Chromium (total)	19.3	
	B22HT7	31.09	102	Lead	15.5	
	B22HT5	25.91	85	Molybdenum	1.24	
	B22HV0	32.49	106.6	Total beta radiostrontium	2.4 (pCi/g)	
199-D7-5	B23RD8	19.35	63.5	Chromium (total)	24.3	
	B23RD8	19.35	63.5	Lead	10.6	
	B23RD8	19.35	63.5	Lithium	15.5	
	B23RD4	12.19	40	Molybdenum	0.48	
	B23RD5	14.05	46.1	Molybdenum	0.61	
	B23RD6	15.45	50.7	Molybdenum	0.74	
	B23RD8	19.35	63.5	Nickel	20.6	
	B23RD5	14.05	46.1	Selenium	1.08	
	B23RD6	15.45	50.7	Selenium	1.16	
	B23RD8	19.35	63.5	Selenium	1.89	
	B23RD8	19.35	63.5	Thallium	0.27	
199-D7-6	B244W2	7.50	24.6	Antimony	1.43	
	B244W2	7.50	24.6	Chromium (total)	655	
	B244W2	7.50	24.6	Copper	95	
	B244W5	13.26	43.5	Manganese	654	
	B244W2	7.50	24.6	Manganese	970	
	B244W3	10.79	35.4	Molybdenum	0.99	
	B244W2	7.50	24.6	Molybdenum	147	
	B244W2	7.50	24.6	Nickel	78.2	
	B244W5	13.26	43.5	Selenium	0.96	
	B244W3	10.79	35.4	Selenium	1.12	
	B244W2	7.50	24.6	Selenium	1.39	
	B244W5	13.26	43.5	Thallium	0.21	
199-D8-89	B22HX1	19.54	64.1	Chromium (total)	203	
	B22HX1	19.54	64.1	Molybdenum	3.07	
	B22HX1	19.54	64.1	Nickel	106	
199-H1-2	B24DF0	16.61	54.5	Selenium	1.32	

Table 4-6. Summary of Detections Above Background from Remedial Process Optimization Wells

Well ID	Sample ID	Sample Bottom Depth (m)	Sample Bottom Depth (ft)	Analyte	Result (in mg/kg unless noted)
199-H1-35	B22HY0	14.63	48	Barium	138
199-H1-36	B23511	14.17	46.5	Barium	160
	B23511	14.17	46.5	Manganese	709
	B23508	11.83	38.8	Molybdenum	0.56
	B23509	14.17	46.5	Molybdenum	0.61
	B23511	14.17	46.5	Selenium	0.85
	B23506	9.60	31.5	Selenium	0.9
	B23509	14.17	46.5	Selenium	1.43
	B23509	14.17	46.5	Antimony	0.46
	B23508	11.83	38.8	Selenium	1.92
199-H1-4	B24DF1	14.97	49.1	Manganese	542
	B24DF1	14.97	49.1	Selenium	0.94

ID = identification

The samples from the RUM were used to determine whether Cr(VI) is leaching out of the RUM as a long-term continuous source and whether the RUM is an effective aquitard for the unconfined aquifer beneath 100-D/H. The permeameter testing results are discussed in Chapter 3, Section 3.6. The analytical results for Cr(VI) are presented in Appendix D, Table D-70. Cr(VI) was not detected in any of the RPO soil samples.

#### 4.3.22 Evaluation of Water Addition to Wells and Boreholes during Sampling

The wells and boreholes installed during the RI field activities at 100-D/H were drilled using the cable tool method or using Foremost AP-1000 diesel-percussion-hammer drill rigs, commonly referred to as Becker Hammer rigs (*Borehole Summary Report for the Installation of 16 Resource Protection Wells in the 100-HR-3 Groundwater Operable Unit in Support of the Integrated 100 Areas RI/FS: 100-D/H Decisional Unit* [SGW-49912]), which is standard practice at the Hanford Site. Periodically, water was added to the hole to allow removal of drill cuttings from the dry, unconsolidated sediments of the Hanford formation and Ringold Formation unit E. The intent is to provide sufficient water for removing cuttings and advancing the borehole without disturbing the underlying material, which is being tested for a variety of mobile and immobile contaminants. An analysis was conducted to evaluate the potential effects to the representativeness of the RI characterization samples (*Data Quality Evaluation of Vadose Zone Soil Sampling Data Collection During RI Drilling for the 100 Area Operable Units* [ECF-100KR4-11-0166]). Typically, one gallon (0.13 ft³) of water was sufficient to provide some cohesion to the cuttings, allowing the sample to be retrieved. However, occasionally 5 to 20 gal (0.67 to 2.67 ft³) were used. Most of the additions were completed at least 0.6 m (2 ft) above the planned split spoon sample interval.

Water was added during drilling at 19 of the 27 wells and borings drilled during the RI to facilitate the removal of cuttings. Well or boring locations with at least one sample that may have been impacted by the

addition of water were: C7855 (one sample), 199-D3-5 (four samples), 199-D5-133 (one sample), 199-D5-143 (six samples), 199-H6-4 (one sample), 199-D5-141 (two samples), 199-D5-134 (four samples).

At these locations, the analytical results for mobile contaminants, such as Cr(VI), were evaluated further. Sample results from the entire thickness of the vadose zone were slightly above or below the detection limits in each of the boreholes with potentially impacted samples. The results were consistent regardless of the addition of water during drilling. This indicates that the sample results were not affected. Evaluation of mobile constituent data from a large number of boreholes does not reveal any particular trends. There are occasional changes up to plus or minus 0.5 mg/kg for Cr(VI), which may be a result of some redistribution during drilling or more likely reflects the actual distribution with depth. Variations appear to be within the bounds of measurement error. The data from sample intervals with added water were consistent with data from internals above and/or below the interval. These observations suggest that the samples provide us with a reasonable and representative estimate of subsurface conditions.

In conclusion, the intent of the drilling was to provide representative samples for physical property and contaminant analysis. Occasionally, the addition of water was required to provide either additional density for the drilling air in the Becker Hammer or cohesion to remove cuttings using the cable tool method so the drilling could progress. Review of the vadose zone conditions indicates that the large matric potentials will tend to wick water preferentially in the lateral direction. This was confirmed in many instances by the neutron logs that measured the presence of higher water content at the depth where water was added. Consequently, it does not appear that the additional water would have significantly contacted the zone of the split-spoon in most of the split-spoon samples collected. While there are samples affected that do increase the uncertainty at some locations, there does not appear to be a bias introduced to these data that would change the conclusions of the nature and extent and fate and transport analyses and would not change the selection of remedies and combination of remedies that are described in the FS.

# 4.3.23 Summary of Vadose Zone Nature and Extent

Soil samples were collected during limited field investigations, interim remedial actions, and the RI to support an evaluation of the nature and extent of existing contamination in the vadose zone at 100-D/H. Soil data from these efforts are used to identify the type, concentration, and distribution of contamination detected (if no background values are available) or present above background concentrations in the vadose zone. The preliminary COPCs identified in Table 4-7 provide an indicator of anthropogenic impacts associated with discharging effluent to the soil and other waste management practices. Various radionuclides, metals, semivolatile organic compounds, volatile organic compounds, PCBs, pesticides, and anions are identified as preliminary COPCs in the vadose zone. Their concentrations and distributions vary by contaminant and location.

Table 4-7. Preliminar	ν Contaminants o	f Potential Concern	Present in the	Vadose Z	one Above Backo	round
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Radionuclides	Metals	Semivolatile Organic Compounds		
Americium-241	Antimony	1,3-Dichlorobenzene	Benzo(k)fluoranthene	
Carbon-14	Arsenic	1,4-Dichlorobenzene	Chrysene	
Cesium-137	Barium	2-Chlorophenol	Dibenzo(a,h)anthracene	
Cobalt-60	Lithium	4-Chloro-3-Methylphenol	Dimethylphthalate	
Europium-152	Cadmium	Acenaphthene	Fluoranthene	
Europium-154	Chromium	Acenaphthylene	Fluorene	

Table 4-7. Preliminary Contaminants of Potential Concern Present in the Vadose Zone Above Background

Radionuclides	Metals	Semivolatile	Organic Compounds
Europium-155	Copper	Anthracene	Indeno(1,2,3cd)pyrene
Neptunium-237	Cr(VI)	Benzo(a)anthracene	Pentachlorophenol
Nickel-63	Lead	Benzo(b)fluoranthene	Phenanthrene
Plutonium-238	Mercury	Benzo(g,h,i)perylene	Pyrene
Plutonium-239/240	Molybdenum	Benzo(a)pyrene	2-Methylnaphthalene
Strontium-90	Nickel	Dibenzofuran	N-Nitrosodiphenylamine
Technetium-99	Selenium	Naphthalene	Anions
Tritium	Silver	Pesticides	Cyanide
Uranium-233/234	Strontium	Aldrin	Fluoride
Uranium-235	Thallium	Beta-BHC	Nitrate
Uranium-238	Tin	Delta-BHC	Nitrite
Polychlorinated	Vanadium	Endrin aldehyde	Sulfate
Biphenyls	Zinc	Endrin ketone	Volatile Organic
Aroclor-1242	Boron	Heptachlor	Compounds
Aroclor-1254		Heptachlor epoxide	4-Methyl-2-Pentanone
Aroclor-1260		4,4-DDT	1,1,1-Trichloroethane

The concentrations of most radionuclides generally decrease with depth. Radionuclides like americium-241, cesium-137, and europium-152 were mainly detected in the upper half of the vadose zone. The distribution of other radionuclides, such as carbon-14, neptunium-237, and technetium-99, are characterized typically as sporadic or single detections. Strontium-90 appears to be the most widespread radionuclide associated with historical 100-D/H sources, extending throughout the vadose zone at some waste sites.

Metals are the second most common group of analytes detected or present above background levels in 100-D/H. Strontium (metal), and tin were consistently detected in RI samples, but their presence reflects the lack of an established background level and does not appear to be indicative of Hanford Site operations. Residual Cr(VI) and total chromium were frequently detected in the vadose associated with remediated waste sites during RI sampling, but the maximum Cr(VI) concentration (4.07 mg/kg) was detected at 116-H-7 at 4.8 m (15.7 ft) bgs and their concentrations both generally decrease with depth. Antimony, barium, boron, cadmium, copper, mercury, selenium, silver, thallium, vanadium, and zinc were only identified at a limited number of waste sites.

PCBs, semivolatile organics, volatile organics, pesticides, and anions are generally present infrequently, at low concentrations, or single detections in the vadose zone.

The mobility and risk associated with contamination in the vadose zone are further evaluated in Chapters 5, 6, and 7 to assess the need for remedial action.

#### 4.4 Groundwater Contamination

This section presents a comprehensive interpretation of results from sampling conducted to address additional data needs for spatial and temporal distribution of contaminants as identified in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). Concentration trends over time and summary statistics for groundwater COPCs are based on groundwater data from wells sampled over a 7-year period (from January 2006 through December 2012). Figure 2-36 of the 100-D/H Work Plan presents the location of the groundwater monitoring wells and the aquifer tubes in 100-D/H area. Effects on contaminant concentrations and distributions from changes in Columbia River stage are discussed.

The 100-D/H Work Plan (DOE/RL-2008-46-ADD1), Section 4.8, identified the following data need associated with evaluation of the spatial and temporal distribution of contaminants in groundwater.

Data Need No. 13: Collect and analyze groundwater samples from select groundwater wells. As a result of the uncertainties identified in the RCBRA Report (DOE/RL-2007-21, Volume II), the Integrated Work Plan (DOE/RL-2008-46-ADD1) added activities that would help reduce uncertainties, verify conclusions of the HHRA presented in the RCBRA Report (DOE/RL-2007-21, Volume II), and ensure that contaminants were not inadvertently overlooked based on the use of the existing groundwater dataset. Section 3.6.5.1 of the Integrated Work Plan (DOE/RL-2008-46) identifies the following activities to reduce uncertainties:

- Identify existing and/or install new monitoring wells that are spatially representative of the groundwater. This set of wells will represent locations where a receptor potentially could contact groundwater.
- Conduct multiple rounds of sampling to obtain temporal representation of the unconfined aquifer
  from influence of river stage. Additional rounds of sampling at spatially representative monitoring
  wells will represent current groundwater conditions and capture the influence of river fluctuations on
  COPC concentrations.
- Analyze all spatially representative monitoring wells for a focused list of groundwater COPCs identified for each round of sampling. Analyzing each of the monitoring wells for COPCs will provide a dataset that is representative of potential releases to the groundwater.
- Evaluate sample results from characterization activities to support final remedial action decisions for groundwater.

To address data gap 13, 52 existing wells were sampled and results were analyzed for spatial and temporal distribution. The sampling locations are presented on Figure 2-3.

The contaminant plume areas are discussed geographically as the 100-D southern plume, 100-D northern plume, 100-H plume, and Horn area plume, and are mainly based on the distribution of Cr(VI) concentrations. The other contaminants are primarily collocated with the Cr(VI) plume. The highest concentrations of contaminants have been identified in the southern plume of 100-D. Slightly lower concentrations are present in the 100-D northern plume and at 100-H. The Horn area plume, which is characterized by even lower contaminant concentrations, is the region between 100-D and 100-H.

For analytes that have shown consistent detections above action levels (sources of action levels are defined in Section 4.4.1.2), plume maps were developed to show the spatial extent of contamination in the unconfined aquifer at 100-D, 100-H, and the Horn. Plume maps were created for Cr(VI), nitrate, strontium-90, zinc, carbon tetrachloride, sulfate, and tritium.

## 4.4.1 Groundwater Data Collected for Spatial and Temporal Analysis

As a result of the uncertainties identified in the RCBRA (DOE/RL-2007-21, Volume II), a rigorous analysis of groundwater data was performed for the purpose of identifying COPCs and reported in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). In total, 31 groundwater COPCs were identified through the activities of the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) and are listed in the 100-D/H SAP (DOE/RL-2009-40), Table 1-2. A total of 52 monitoring wells were selected to represent the 100-HR-3 Groundwater OU spatially; three sampling rounds were collected from each location for those analytes identified as COPCs. The sampling rounds were collected at low, transitional, and high river stage to represent the temporal variability in aquifer constituent concentrations during the year.

Seasonal variations in river stage affect aquifer conditions by causing temporary changes in the water table. These elevation changes affect flow directions and rates, causing local changes in contaminant concentrations. For example, high river stage conditions may cause an influx of clean water from the river, thereby lowering contaminant concentrations. When the aquifer further inland experiences the high river elevation as a pressure pulse, the higher water table may affect a contaminated section of unsaturated sediments, causing contaminant concentrations to rise. Conversely, when the river stage is at the lowest levels, the groundwater flow direction near the river is generally toward the river, also causing contaminant plumes to migrate toward the river. Further inland, contaminant concentrations in the aquifer may decrease because contaminated soils are above the water table and, therefore, cannot interact with groundwater to release contaminants. To characterize the dynamic groundwater conditions and associated contaminant levels adequately, sampling was conducted during periods when the river stage and water table are high, when both are low, and at some interval between or transitional to extreme conditions.

The Columbia River stage at the 100-D Area gage can vary 3 to 4 m (9.8 to 13.1 ft) between low and high elevation, which is based on a 30-day moving average selected to show the influence that river dynamics have on groundwater levels. This can cause water table fluctuations of several meters, depending on the hydraulic properties of local sediments and the distance of the observation point from the river. Examples of seasonal river changes are shown on Figure 4-63. The daily averaged elevations depict a cyclic pattern of maximum to minimum river stage from year to year. These periodic or cyclic changes are engineered by upstream dams and reservoirs used for flood control, hydroelectric production, and salmon spawning programs. For any given year, the highest river stages occur from May through June while the lowest levels occur from September through October, possibly to mid-November. The intervals between the maximum and minimum river stage from approximately December through April and July through August are periods when the aquifer is in transition. The change from low to high elevations occurs gradually over about four months, when levels are increasing from the low in the fall of the year to the June/July maximum. The change from high to low levels is sharp, occurring over a two-month interval through July and August.

To illustrate that the maximum and minimum river stages are predictable and, therefore, useful for setting the 100-HR-3 OU risk assessment sampling schedule, trends of daily averaged elevation measurements covering the same 360-day period from September through August of the following year are superimposed on Figure 4-64. For example, data from September 1, 2005 is overlain on data from September 1, 2006 and September 1, 2007. Such a comparison illustrates the repeatable cycle of seasonal variations, allowing the timing of river fluctuations to set the schedule for the 100-HR-3 OU RI groundwater sampling. This schedule, as discussed in the Integrated Work Plan (DOE/RL-2008-46, ADD1), began in October 2009 and was completed in June 2010.

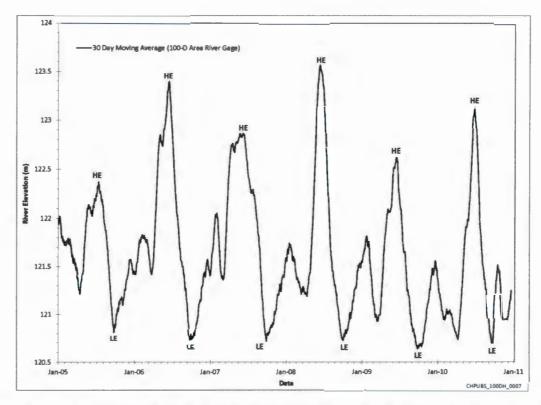


Figure 4-63. Seasonal Fluctuations in River Elevations Illustrating the Cyclic Nature of Maximum High and Low Elevations Over Multiple Years

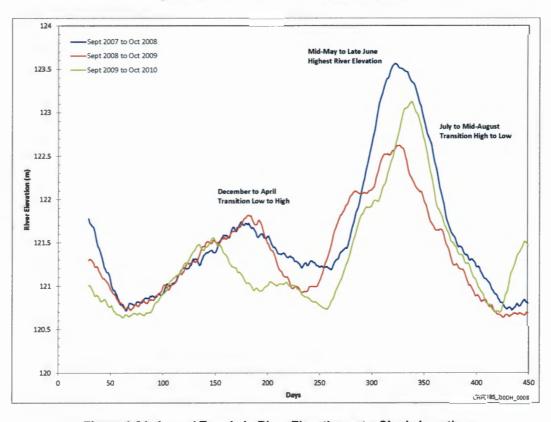


Figure 4-64. Annual Trends in River Elevations at a Single Location

With this prescribed period over which groundwater samples could be collected, the water table was low in October 2009, and at or near a maximum in June 2010. The transitional period occurred during the winter of 2009 to 2010 through the early spring of 2010. Thus, sampling of the groundwater network was scheduled in October 2009, March 2010, and June 2010. The final sampling intervals based on actual sampling dates are compared to a trend line of river elevation data on Figures 4-63 and 4-64. First, each sampling event was completed within the predetermined periods for low water table from mid-September to mid-November, transitional aquifer conditions occurring from December 2009 through April 2010, and maximum aquifer levels from May through June 2010. It should be noted, however, that an extremely high river stage occurred in July 2010. This anomaly was a result of unusual snowfall and temperatures, and could not have been predicted. Second, each sampling event was completed within 30 days, thus minimizing effects from dynamic river fluctuations. Based on the previous discussion, the chemistry data from groundwater samples collected during these three sampling events are fully representative of the dynamic groundwater conditions at the 100-HR-3 OU.

In monitoring wells, the water table response becomes more muted as distance from the river increases. Figures 4-65 and 4-66 show hydrographs for river gages at 100-D and 100-H, and adjacent wells screened in the unconfined aquifer. Groundwater levels in well 199-D8-70 are fairly close to that of the river elevation versus wells 199-D2-11 and 199-D5-99, where the groundwater level responses are much more seasonal. Similar responses are observed in 100-H, but the hydraulic conductivity of the aquifer matrix is higher, causing the wells to be in much higher hydraulic communication with the river. Groundwater level responses in these wells tend to follow the river more closely. Further inland at well 199-H5-1A, the response is more muted. Overall, the response of the river can be measured relatively far inland in the aquifer.

The analytical data are presented in Appendix D, incorporated into the historical summary statistics, and included in the contaminant distribution discussions. Further evaluations of this dataset, including the evaluations of COPCs, are presented in Chapter 6, Human Health Risk Assessment.

#### 4.4.1.1 Historical Groundwater Evaluation

Uncertainties associated with the groundwater dataset were identified in the RCBRA. These uncertainties relate to the ability of the groundwater dataset collected from 1992 to 2008 to represent current baseline conditions and potential exposure within each groundwater OU. Analytical data used for the screening level assessment were collected to fulfill a variety of state and federal regulations, including the *Atomic Energy Act of 1954*, RCRA, CERCLA, and Section 173 of the *Washington Administrative Code*. Although the monitoring data can be used for risk assessment purposes, there are uncertainties associated with its use. Specifically, target analytes, sampling frequencies, and MDLs (or reporting limits) are different between programs because the information is used to meet different requirements.

As a result of the uncertainties identified in the RCBRA (DOE/RL-2007-21, Vol II), a rigorous analysis of groundwater data for the purpose of identifying COPCs was performed in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). The groundwater dataset used for COPC identification consisted of sampling and analysis data collected from 98 monitoring wells from the 100-HR-3 Groundwater OU. The sampling and analysis data were collected between January 7, 1992, and November 20, 2008, and include four consecutive quarterly rounds collected during 1992 and 1993 and reported in the 100-HR-3 LFI (DOE/RL-93-43), which were also used for the ecological component of the qualitative risk assessment (Qualitative Risk Assessment for the 100-HR-3 Groundwater Operable Unit [WHC-SD-EN-RA-007]).

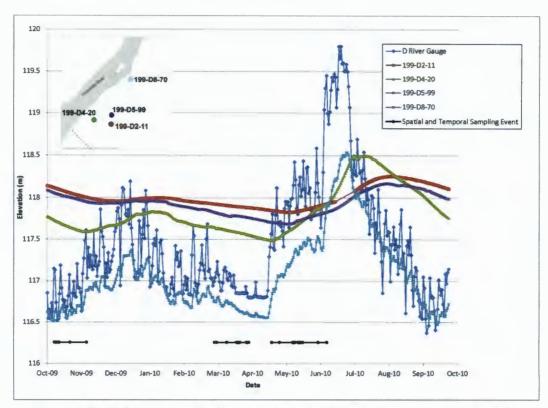


Figure 4-65. Hydrographs of the Columbia River at 100-D and Groundwater Levels in Adjacent Monitoring Wells

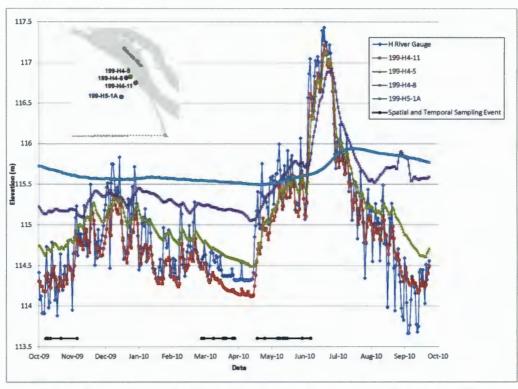


Figure 4-66. Hydrographs of the Columbia River at 100-H and Groundwater Levels in Adjacent Monitoring Wells

In total, 31 groundwater COPCs were identified through the activities of the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) and are listed in the 100-D/H SAP (DOE/RL-2009-40), Table 1-2. The process used to develop the vadose zone soil target analyte lists and groundwater COPCs is described in Section 4.4 of the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). Step 4 of the COPC identification process identifies the agency review of monitoring well locations and groundwater COPCs. This step of the process allows the agency to adjust the COPC identification process by adding additional analytes or sample locations on a site-specific basis. Table 4-8 lists the additional analytes and the monitoring well locations that were included as a result of Step 4 of the COPC identification process.

Table 4-8. Additional Groundwater Analytes and Locations for Analysis

Pesticides by Method 8081	PCBs by Method 1668A	PCBs by Method 8082	Polynuclear Aromati Hydrocarbons by Method 8310
199-D5-15 <sup>a</sup>	199-D5-15 <sup>a</sup>	199-D4-84 <sup>a</sup>	199-D4-84 <sup>a</sup>
199-D8-71 <sup>b</sup>	199-D8-55 <sup>b</sup>	199-D5-13 <sup>a</sup>	199-D5-13 <sup>a</sup>
	199-D8-71 <sup>b</sup>	199-D5-15 <sup>a</sup>	199-D5-15 <sup>a</sup>
	199-H4-10 <sup>a</sup>	199-D5-17 <sup>a</sup>	199-D5-17 <sup>a</sup>
	199-H4-13 <sup>a</sup>	199-D5-99 <sup>a</sup>	199-D5-99 <sup>a</sup>
	199-H4-48 <sup>a</sup>	199-D8-55 <sup>b</sup>	199-D8-55 <sup>b</sup>
		199-D8-71 <sup>b</sup>	199-D8-71 <sup>b</sup>
		199-D8-88 <sup>a</sup>	199-D8-88 <sup>a</sup>
		199-H3-2A <sup>a</sup>	199-H3-2A <sup>a</sup>
		199-H4-3 <sup>b</sup>	199-H4-3 <sup>b</sup>
		199-H4-10 <sup>a</sup>	199-H4-10 <sup>a</sup>
		199-H4-11 <sup>b</sup>	199-H4-11 <sup>b</sup>
		199-H4-13 <sup>a</sup>	199-H4-13 <sup>a</sup>
		199-H4-16 <sup>a</sup>	199-H4-16 <sup>a</sup>
		199-H4-45 <sup>b</sup>	199-H4-45 <sup>b</sup>
		199-H4-48 <sup>a</sup>	199-H4-48 <sup>a</sup>
	nnic Compounds by od 8270	Radionuclides <sup>c</sup>	Cyanide by Method 9012
199-D4-84 <sup>a</sup>	199-H3-2A <sup>a</sup>	All wells in monitoring	199-H4-3 <sup>b</sup>
199-D5-13 <sup>a</sup>	199-H4-3 <sup>b</sup>	well network.	
199-D5-15 <sup>a</sup>	199-H4-10 <sup>a</sup>		
199-D5-17 <sup>a</sup>	199-H4-11 <sup>b</sup>		
199-D5-99 <sup>a</sup>	199-H4-13 <sup>a</sup>		
199-D8-55 <sup>b</sup>	199-H4-16 <sup>a</sup>		
199-D8-71 <sup>b</sup>	199-H4-45 <sup>b</sup>	1	
199-D8-88 <sup>a</sup>	199-H4-48 <sup>a</sup>		

a. Collected at the low river stage

The analytical performance requirements (required analytical method) and the lowest chemical-specific ARAR are listed in the 100-D/H SAP (DOE/RL-2009-40). The action level is listed to ensure that the

b. Collected at the low river stage and high river stage

c. Radionuclides include gross alpha, gross beta, cesium-137, cobalt-60, europium-152, and europium-154.

PCB = polychlorinated biphenyl

estimated quantitation limit (EQL) is adequate for confirming the presence or absence of the COPC at the corresponding level. In total, 52 monitoring wells were selected to represent the 100-HR-3 Groundwater OU spatially; three sampling rounds were collected from each location for those analytes identified as COPCs and radionuclides listed in Table 1-2 of the 100-D/H SAP (DOE/RL-2009-40). The sampling rounds were collected at low, transitional, and high river stage to represent the temporal variability in aquifer constituents during the year. This dataset was used to perform the risk assessment presented in Chapter 6.

## 4.4.1.2 Groundwater Evaluation for the Unconfined Aquifer

The nature and extent of contamination in groundwater was based on the last seven years of data, which were considered representative of current groundwater conditions (that is, samples collected between January 1, 2006 and December 31, 2012). The nature and extent evaluation uses a subset of data from the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) for wells screened in the unconfined aquifer, as well as all spatial and temporal wells considered in the groundwater risk assessment. A total of 208 wells, including 52 wells sampled to better refine the spatial and temporal aspects of contaminant distribution, were considered. Figure 4-67 and Figure 4-68 provide the locations of wells considered in the groundwater evaluation for the 100-D Area, 100-H Area, and the treatability test areas. Groundwater data for 100-D/H were compiled and statistically analyzed and the results are presented in Appendix N, Table N-1 through Table N-3. These tables present the summary statistics for each analyte identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) and the 100-D/H SAP (DOE/RL-2009-40) and list the background concentrations in Hanford Site groundwater (*Hanford Site Background: Part 3, Groundwater Background* [DOE/RL-96-61]) where available, and the action level for each analyte.

The additional analytes that were requested for each well listed in Table 4-8 are presented in Appendix N, Table N-4 through Table N-19. These tables list the additional analytes by well, provide summary statistics (where applicable), and list the background concentrations and action level for each analyte.

For the purpose of COPC identification, action levels are screening levels derived from chemical-specific ARARs and/or risk based concentrations using default exposure assumptions (it should be noted that some of the exposure pathways in these screening levels are incomplete).

Following are the sources of action levels from federal regulations:

- 40 CFR 141, "National Primary Drinking Water Regulations," MCLs, secondary MCLs, and nonzero MCLGs established under the Safe Drinking Water Act of 1974 (SDWA)
- National Recommended Water Quality Criteria, Ambient Water Quality Criteria (AWQC) established under Section 304 of the Clean Water Act of 1977
- "Water Quality Standards" (40 CFR 131) for states not complying with Section 303 of the *Clean Water Act of 1977*

Following are the sources of the action levels from Washington State regulations:

- "Water Quality Standards for Surface Waters of the State of Washington" (WAC 173-201A)
- "Groundwater Cleanup Standards" (WAC 173-340-720)
- "Group A Public Water Supplies," "Maximum Contaminant Levels (MCLs) and Maximum Residual Disinfectant Levels (MRDLs)" (WAC 246-290-310)

While surface water and AWQC standards are considered for the identification of action levels, it must be noted that these standards only apply for groundwater where it enters the Columbia River. For the upland parts of groundwater, only DWSs are applicable.

The following evaluation specifically identifies when the action level is a DWS or an AWQC. The evaluation presented in this section focuses on the following analytes:

- Analytes that are identified as COPCs in the groundwater risk assessment provided in Section 6.3 that warrant further evaluation in the FS.
- Analytes identified as historical COPCs in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) as a result of uncertainties resulting from limitations in the analytical data (inadequate MDLs or anomalous results). Analytical data used in the groundwater risk assessment provided in Section 6.3 and data from a larger population of wells sampled over a longer sampling period were evaluated to determine these analytes do not warrant further evaluation in the FS.
- Additional analytes that were identified through Step 4 of the COPC identification process in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) and do not warrant further evaluation in the FS.

**COPCs Warranting Further Evaluation in FS.** Section 6.3 identifies the COPCs that warrant further evaluation in the FS for each of the exposure areas evaluated in the groundwater risk assessment. The COPCs are discussed in the following paragraphs as applicable to each exposure area (100-D Area, 100-H Area, and the Horn area).

**100-D Area.** Cr(VI), chromium, and nitrate are identified in the 100-D Area as COPCs that warrant further evaluation in the FS. Concentrations of these COPCs are widely distributed and consistently present above the DWS (nitrate) or the state surface water quality standard or AWQC (Cr(VI) and chromium). The following paragraphs provide a summary for each COPC. Additional information regarding trend plots and contours is provided in Section 4.5.

Cr(VI) was reported above the state surface water quality standard (WAC 173-201A) of 10  $\mu$ g/L in 89 percent of the detected unfiltered results and 92 percent of the detected filtered results. Although all monitoring wells within the 100-D Area were compared to the state surface water quality standard value of 10  $\mu$ g/L, this standard only applies for groundwater where it enter the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L. Concentrations of filtered Cr(VI) ranged between 2.0 and 69,700  $\mu$ g/L. With the exception of two unfiltered results, all MDLs were less than or equal to 10  $\mu$ g/L. Note that an August 2010 groundwater sample from Well 199-D5-122, reports the site maximum Cr(VI) concentration of 69,700  $\mu$ g/L. This well is located in the 100-D southern plume.

Chromium (total) was detected in 97 percent of the unfiltered and filtered groundwater samples. Chromium (total) was reported above the AWQC of 65  $\mu$ g/L in 63 percent of the detected unfiltered results and 60 percent of the detected filtered results. Although all monitoring wells within the 100-D Area were compared to the AWQC value of 65  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. Concentrations of unfiltered chromium (total) range between 3.9 and 61,100  $\mu$ g/L and filtered chromium (total) ranged between 3.4 and 10,500  $\mu$ g/L. All MDLs were less than the AWQC of 65  $\mu$ g/L.

Nitrate was detected in 100 percent of the unfiltered groundwater samples. Nitrate was reported above the DWS of  $45,000 \,\mu\text{g/L}$  in 41 percent of the detected unfiltered results. Concentrations of unfiltered nitrate ranged between 1,810 and  $107,000 \,\mu\text{g/L}$ .

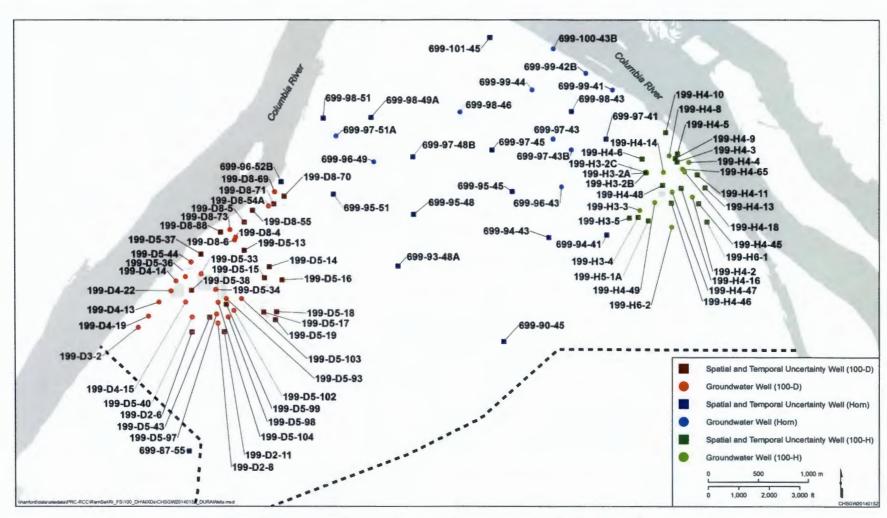


Figure 4-67. Well Locations Used in the Groundwater Evaluation for the Unconfined Aquifer

Figure 4-68. Well Locations of In Situ Treatability Tests at 100-D/H used in the Groundwater Evaluation

**100-H Area**. Cr(VI), strontium-90, and nitrate are identified in the 100-H Area as COPCs that warrant further evaluation in the FS. Concentrations of Cr(VI) and strontium-90 are widely distributed and consistently present at concentrations above the state surface water quality standard (Cr(VI)) or the DWS (strontium-90). Nitrate and uranium in the 100-H Area are not widely distributed but are present at concentrations above the DWS in localized areas. The following paragraphs provide a summary for each COPC. Additional information regarding trend plots and contours are provided in Section 4.5.

Cr(VI) was detected in 91 percent of the unfiltered and 89 percent of the filtered groundwater samples. Cr(VI) was reported above the state surface water quality standard (WAC 173-201A) of 10  $\mu$ g/L in 60 percent of the detected unfiltered results and 50 percent of the detected filtered results. Concentrations of filtered Cr(VI) ranged between 2 and 75  $\mu$ g/L. All MDLs were less than the state surface water quality standard of 10  $\mu$ g/L. Although all monitoring wells within the 100-H Area were compared to the state surface water quality standard value of 10  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L.

Strontium-90 was detected in 50 percent of the unfiltered groundwater samples. Strontium-90 was reported above the DWS of 8 pCi/L in 32 percent of the detected unfiltered results. Concentrations of unfiltered strontium-90 ranged between 1.1 pCi/L and 110 pCi/L. All MDLs were less than the DWS of 8 pCi/L.

Nitrate was detected in 100 percent of the unfiltered groundwater samples. Nitrate was reported above the DWS of  $45,000~\mu g/L$  in 6.2 percent of the detected unfiltered results. Concentrations of unfiltered nitrate ranged between 416 and  $253,000~\mu g/L$ . The maximum nitrate concentration of  $253,000~\mu g/L$  was measured in well 199-H4-3 during May 2006. Nitrate concentrations measured at 199-H4-3 during 2010 and 2012 range between 27,400 and  $74,400~\mu g/L$ .

Horn Area. Cr(VI) and chromium are identified in the Horn area as COPCs that warrant further evaluation in the FS. Concentrations of these COPCs are widely distributed and consistently present at concentrations above the state surface water quality standard or AWQC (Cr(VI) and chromium). The following paragraphs provide a summary for each COPC. Additional information regarding trend plots and contours are provided in Section 4.5.

Cr(VI) was detected in 87 percent of the unfiltered and filtered groundwater samples. Cr(VI) was reported above the state surface water quality standard (WAC 173-201A) of 10  $\mu$ g/L in 87 percent of the detected unfiltered results and 89 percent of the detected filtered results. Concentrations of filtered Cr(VI) ranged between 2.9 and 117  $\mu$ g/L. All MDLs were less than the state surface water quality standard of 10  $\mu$ g/L. Although all monitoring wells within the Horn area were compared to the state surface water quality standard of 10  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L.

Chromium (total) was detected in 90 percent of the unfiltered and filtered groundwater samples. Chromium (total) was reported above the AWQC of 65  $\mu$ g/L in 15 percent of the detected unfiltered results and 13 percent of the detected filtered results. Concentrations of filtered chromium (total) ranged between 4.3 and 113  $\mu$ g/L. All MDLs were less than the AWQC of 65  $\mu$ g/L. Although all monitoring wells within the groundwater Horn area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of  $100~\mu$ g/L.

*Historical COPCs—Nondetected.* Historical COPCs are those analytes that were identified in the 100-D/H SAP (DOE/RL-2009-40) or those analytes for which a maximum concentration exceeding an action level

was reported during the spatial and temporal sampling (Section 6.3). The following provides descriptions of those historical COPCs that were not detected in the spatial and temporal dataset or the dataset representing a larger population of wells and a longer sampling timeframe. Nondetected historical COPCs include radionuclides and VOCs.

Gross gamma analytes (cesium-137, cobalt-60, europium-152, and europium-154) were identified as additional analytes in the 100-D/H SAP (DOE/RL-2009-40). Gross gamma analytes were analyzed in all of the RI monitoring network wells during all sampling rounds. Gross gamma analytes were not detected in any of the groundwater samples analyzed from any area. All MDLs were less than their respective DWSs. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, gross gamma analytes are not retained as COPCs to be further evaluated in the FS.

1,1-Dichloroethene was identified as a historical COPC in the 100-D/H SAP (DOE/RL-2009-40) not because it was detected but because the laboratory MDLs were not adequate for determining its presence at the action level. The action level for 1,1-dichloroethene 7  $\mu$ g/L and is based on the DWS. 1,1-Dichloroethene was not detected in any groundwater sample from any area and all MDLs are less than the DWS. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, 1,1-dichloroethene is not retained as a COPC for further evaluation in the FS.

Benzene was identified as a historical COPC in the 100-D/H SAP (DOE/RL-2009-40) because it was detected above the groundwater cleanup standard and most MDLs were greater than the groundwater cleanup standard. Benzene was not detected in any unfiltered groundwater sample from any area. The action level for benzene of  $0.8~\mu\text{g/L}$  is based on the 2007~MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) level. However, the analytical method cannot attain the action level for benzene; therefore, nondetected concentrations are reported at the EQL of  $1.5~\mu\text{g/L}$  identified in the 100-D/H SAP (DOE/RL-2009-40). Benzene was not detected in any groundwater sample from any area and all MDLs are less than the EQL listed in the 100-D/H SAP (DOE/RL-2009-40). Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, benzene is not retained as a COPC for further evaluation in the FS.

Trichloroethene was identified as a historical COPC in the 100-D/H SAP (DOE/RL-2009-40) not because it was detected but because the MDLs were not adequate for determining its presence at or below the action level. The action level for trichloroethene of 0.95  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Trichloroethene was not detected in any groundwater sample from the 100-D or 100-H Areas, and all MDLs are less than or equal to the action level. Trichloroethene was detected in three samples within the Horn area; however, all concentrations were less than the action level. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, trichloroethene is not retained as a COPC for further evaluation in the FS.

Vinyl chloride was identified as a historical COPC in the 100-D/H SAP (DOE/RL-2009-40) not because it was detected but because the MDLs were not adequate for determining its presence at or below the action level." The action level for vinyl chloride of 0.061  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. However, the analytical method cannot attain the action level for vinyl chloride; therefore, nondetected concentrations are reported at the EQL of 5  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Vinyl chloride was not detected in any groundwater sample from any area and all MDLs are less than the EQL listed in the 100-D/H SAP (DOE/RL-2009-40). Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, vinyl chloride is not retained as a COPC for further evaluation in the FS.

Historical COPCs—100-D Groundwater Area. The following subsections describe historical COPCs that were detected at least once in the 100-D groundwater area and include radionuclides, VOCs, anions, and metals. As described earlier, historical COPCs are either those analytes that were identified as COPCs in the 100-D/H SAP (DOE/RL-2009-40) or those analytes for which a maximum concentration exceeding an action level was reported during the spatial and temporal sampling (Section 6.3). Summary statistics for groundwater within the 100-D Area are shown in Appendix N (Table N-1).

Radionuclides. Gross alpha and gross beta were identified as additional analytes in the 100-D/H SAP (DOE/RL-2009-40). Gross alpha and gross beta were analyzed in all of the RI monitoring network wells during all sampling rounds as well as in the larger populations of wells over the longer timeframe. Gross alpha was detected in 21 percent of the unfiltered groundwater samples and gross beta was detected in 85 percent of the unfiltered samples. Gross alpha was detected at concentrations ranging between 1.4 and 24 pCi/L. Except for a single detection of gross alpha above the DWS of 15 pCi/L that was measured at 199-D5-93, all measured concentrations were less than the DWS. Gross alpha was measured five times at 199-D5-93; the previous and subsequent sample rounds were less than the DWS suggesting the single detection above the DWS is not associated with an upward trend. Gross beta was detected at concentrations ranging between 2.3 and 152 pCi/L. Gross beta concentrations are consistent with the presence of tritium and strontium-90. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, gross alpha and gross beta are not identified as COPCs to be further evaluated in the FS.

Strontium-90 was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of 8 pCi/L. Strontium-90 was detected in 30 of 135 (22 percent) of the unfiltered groundwater samples, with concentrations ranging between 0.48 and 45 pCi/L. Strontium-90 was measured above the DWS in wells 199-D5-132 and 199-D5-142. Well 199-D5-132 was installed during the RI to fill data gap 2 and data gap 5; concentrations at this well ranged between 25 and 45 pCi/L during 2011 and 2012. Concentrations of strontium-90 at well 199-D5-142 range between 23 and 30 pCi/L during 2012. Additionally, well 199-D5-12, located south of the 116-D-1A liquid waste stream, historically reported strontium-90 concentrations above the DWS (with concentrations up to 52.6 pCi/L) until it was decommissioned in 2002. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, strontium-90 is retained as a COPC for further evaluation in the FS.

Technetium-99 was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of 900 pCi/L. Technetium-99 was detected in 2 of 78 (2.6 percent) of the unfiltered groundwater samples with concentrations ranging between 7.6 and 12 pCi/L. All results (detected concentrations and MDLs) were less than the DWS of 900 pCi/L. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, technetium-99 is not retained as a COPC for further evaluation in the FS.

Tritium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of 20,000 pCi/L. Tritium was detected in 172 of 220 (78 percent) of the unfiltered groundwater samples with concentrations ranging between 180 and 19,000 pCi/L. All results (detected concentrations and MDLs) are less than the DWS of 20,000 pCi/L. Tritium was reported at 199-D5-40 with concentrations that range between 1,400 in 2006 and increasing to 19,000 pCi/L in 2012 and decreasing to 5,800 pCi/L in 2013. Tritium was below the DWS of 20,000 pCi/L at all other monitoring wells. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, tritium is not retained as a COPC for further evaluation in the FS.

Volatile Organic Compounds. Carbon tetrachloride was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for carbon tetrachloride is 0.63 µg/L based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. However, the analytical method cannot attain the action level for carbon tetrachloride; therefore, nondetected concentrations are reported at the EQL of 1 µg/L identified in the 100-D/H SAP (DOE/RL-2009-40). Carbon tetrachloride was detected twice in 199-D2-6 with values of 1.7 µg/L on 8/28/2009 (transitional river stage) and 2.6 µg/L on 10/8/2010 (low river stage), both at concentrations greater than the action level. Well 199-D2-6 (see Figure 4-67 for well location) was sampled and analyzed for carbon tetrachloride during a subsequent transitional river stage (3-30-2010) for the spatial and temporal sampling (0.063 U) and again in May 2010 (0.12 U); both results were nondetected and reported below the action level. No other carbon tetrachloride results were reported for 199-D2-6 during a low river stage. Carbon tetrachloride was detected once in 199-D5-18 (2.7 µg/L) at a concentration greater than the action level. Carbon tetrachloride was analyzed in four subsequent sampling rounds at this well and reported as nondetected concentrations less than the action level or the EQL. All MDLs are less than or equal to the EQL listed in the 100-D/H SAP (DOE/RL-2009-40). The presence of carbon tetrachloride at well 199-D2-6 and 199-D5-18 are not associated with a trend. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, carbon tetrachloride is not retained as a COPC for further evaluation in the FS.

Chloroform was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. MDLs were not adequate for determining the presence of chloroform at or below the action level of 1.4  $\mu$ g/L. The action level for chloroform is 1.4  $\mu$ g/L based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. However, the analytical method cannot attain the action level for chloroform; therefore, nondetected concentrations are reported at the EQL of 5  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Chloroform concentrations above the EQL of 5  $\mu$ g/L were reported in four wells (199-D5-13, 199-D5-38, 199-D8-5, and 199-D8-88). Chloroform concentrations above the EQL were reported in three of nine sampling rounds and does not appear to be associated with a trend at 199-D8-5; concentrations range from less than 1 to 8.3  $\mu$ g/L. Infrequent detections of chloroform at concentrations above the EQL were reported at 199-D5-13 (one of four sampling rounds; 3.1 to 6.4  $\mu$ g/L), 199-D5-38 (one of four sampling rounds; 1.9 to 5.8  $\mu$ g/L), and 199-D8-88 (two of four sampling rounds; 3.2 to 8  $\mu$ g/L). All MDLs are less than the EQL of 5  $\mu$ g/L. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, chloroform is retained as a COPC for further monitoring.

Anions. Fluoride was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and some MDLs were greater than the action level of 960  $\mu$ g/L. The action level of 960  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Fluoride was detected in 186 of 441 (42 percent) of unfiltered groundwater samples with concentrations ranging between 14  $\mu$ g/L and 200  $\mu$ g/L. All fluoride results are less than the action level. Fluoride concentrations in unfiltered samples are also less than the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, fluoride is not retained as a COPC for further evaluation in the FS. Note that although fluoride is not retained as a COPC for further monitoring in this exposure area, fluoride is retained as a COPC for further monitoring in the 100-D ISRM exposure area discussed in Section 4.4.1.4.

Nitrite was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS, and some MDLs were greater than the DWS of 3,300 µg/L.

Nitrite was detected in 93 of 437 (21 percent) of unfiltered samples with concentrations ranging between 39 and 2,400  $\mu$ g/L. All results (detected concentrations and MDLs) were less than the DWS of 3,300  $\mu$ g/L. Nitrite concentrations in unfiltered samples are also greater than the 90<sup>th</sup> percentile Hanford Site background level of 94  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, nitrite is not retained as a COPC. Note that although nitrite is not retained as a COPC for further monitoring in this exposure area, nitrite is retained as a COPC for further monitoring in the 100-D ISRM exposure area discussed in Section 4.4.1.4 (see Table 4-14).

Sulfate was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the secondary DWS of 250,000  $\mu$ g/L. Sulfate was detected in 100 percent of unfiltered groundwater samples with concentrations ranging between 11,000 and 205,000  $\mu$ g/L. All sulfate concentrations were below the secondary DWS of 250,000  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, sulfate is not retained as a COPC. Note that although sulfate is not retained as a COPC for further monitoring in this exposure area, sulfate is retained as a COPC for further monitoring in the 100-D ISRM exposure area discussed in Section 4.4.1.4 (see Table 4-14).

**Metals.** Antimony was identified as a historical COPC in the 100-D/H Work Plan (DGE/RL-2008-46-ADDÍ) because it was detected above the action level, and most MDLs were greater than the action level. The action level for antimony is 6 µg/L based on the DWS. Antimony was detected in 11 of 270 unfiltered samples (4.1 percent) and 9 of 255 (3.5 percent) of the filtered groundwater samples. Antimony concentrations in unfiltered and filtered groundwater samples range between 0.65 and 78 µg/L. Unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. MDLs for results reported by Method 6010 range between 4 and 720 µg/L and detected concentrations range between 4.9 and 78 µg/L. All but one filtered and four unfiltered antimony result reported by Method 6010 were flagged with a "B" qualifier. The "B" qualifier indicates the analyte was detected at a value less than the required detection limit, but greater than or equal to the MDL. Samples collected for the RI were analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40). MDLs for these samples range between 0.3 and 0.6 µg/L and the two detected concentrations range between 0.65 and 1.5 µg/L. Both of the detected concentrations were flagged with a "C" laboratory qualifier indicating that the analyte was detected in both the sample and the associated QC blank, and the sample concentration was less than or equal to five times the blank concentration The results of this evaluation indicate that antimony has historically been detected in groundwater samples at a low frequency (4.1 percent in unfiltered samples and 3.5 percent in filtered samples) with concentrations up to 12 times greater than the action level. All historical detections of antimony are flagged with a "B" qualifier. Antimony concentrations are not associated with a specific location or a trend. Antimony concentrations associated with samples collected for the RI are not above the DWS of 6 μg/L. With the exception of five sample results flagged with a "B" laboratory qualifier and one unqualified result (57 μg/L), all antimony concentrations are below the 90th percentile Hanford Site background level of 55 µg/L. Antimony results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the DWS or the Hanford Site background value. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, antimony is retained as a COPC for further monitoring.

Arsenic was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level and all MDLs were greater than the action level. MDLs were not adequate for determining the presence of arsenic at or below the action level of  $0.058~\mu g/L$ . The action level for arsenic of  $0.058~\mu g/L$  is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. However, the analytical method cannot attain the action

level; therefore, nondetected concentrations are reported at the EQL of 4  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Arsenic was detected in 115 of 119 (97 percent) of the unfiltered and 96 of 106 (91 percent) of the filtered groundwater samples. Arsenic concentrations range between 0.58 and 3.6  $\mu$ g/L in unfiltered and filtered groundwater samples. Minimum, maximum, and 90<sup>th</sup> percentile concentrations for (filtered) background concentrations of arsenic are 0.5, 8.8, and 7.85  $\mu$ g/L, respectively. Arsenic concentrations in unfiltered and filtered samples are less than the 90<sup>th</sup> percentile Hanford Site background concentration. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, arsenic is not retained as a COPC for further evaluation in the FS.

Beryllium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS, and most MDLs were greater than the DWS of 4  $\mu$ g/L. Beryllium was detected in 5 of 262 (1.9 percent) of the unfiltered samples and in 3 of 255 (1.2 percent) of the filtered groundwater samples. Beryllium concentrations in unfiltered and filtered groundwater samples range between 0.092 and 0.31  $\mu$ g/L. All beryllium results (detected concentrations and MDLs) are less than the DWS of 4  $\mu$ g/L. In addition, all beryllium concentrations are less than the 90<sup>th</sup> percentile Hanford Site background level of 2.3  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC and most MDLs were greater than the AWQC of 0.25 µg/L. Cadmium was detected in 3 of 270 (1.1 percent) of the unfiltered samples and was not detected in any of the 255 filtered groundwater samples. Cadmium concentrations in unfiltered groundwater samples range between 0.11 and 1.7 µg/L. Although all monitoring wells within the groundwater area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 5 µg/L. Unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. MDLs for results reported by Method 6010 range between 0.91 and 30 μg/L and a single detection of 1.7 μg/L (flagged with a "B" laboratory qualifier) is also reported by Method 6010. With the exception of 21 of 389 MDLs, all cadmium results (detected concentrations and MDLs) were less than the DWS. All MDLs reported by Method 6010 for filtered samples were greater than the AWQC. Samples collected for the RI used trace methods identified in the 100-D/H SAP (DOE/RL-2009-40). MDLs for samples analyzed by trace methods range between 0.05 and 0.2 µg/L and two detected concentrations ranged between 0.11 and 0.22 µg/L (flagged with a "B" laboratory qualifier") were also reported by Method 200.8. All MDLs reported by Method 200.8 are less than the AWQC. Cadmium results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the AWQC or the 90<sup>th</sup> percentile Hanford Site background level of 0.92 µg/L, and some MDLs cannot attain the DWS. Results indicate that cadmium concentrations above the AWQC are not associated with a specific location or with a trend. All but one detected concentration (1.7 µg/L) of cadmium in unfiltered and filtered samples are below the 90<sup>th</sup> percentile Hanford Site background level of 0.92 µg/L. However, the MDLs reported using Method 6010 do not have sufficient accuracy to attain the Hanford Site background value. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, cadmium is retained as a COPC for further monitoring.

Cobalt was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and some MDLs were greater than the action level. The action level for cobalt of  $4.8~\mu$ g/L is based on the 2007~MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Cobalt was detected in 39 of 270 (14 percent) of unfiltered samples and 39 of 255 (15 percent) of filtered groundwater samples. Cobalt concentrations in unfiltered and filtered groundwater samples range between 0.099 and  $32~\mu$ g/L. Unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010.~MDLs for results

reported by Method 6010 range between 2 and 70 µg/L (43 of 360 greater than action level), unfiltered and filtered concentrations ranged between 0.58 and 32 µg/L (26 of 29 results greater than action level). All but one cobalt result reported by Method 6010 were either flagged with a "B" qualifier (13 of 29 results) or flagged with a "C" qualifier (16 of 29 results). The "C" qualifier indicates that the analyte was detected in both the sample and the associated QC blank, and the sample concentration was less than or equal to five times the blank concentration. Cobalt concentrations for unfiltered and filtered samples flagged with a "B" ranged between 0.58 and 19 µg/L (10 of 13 results above action level). Cobalt concentrations for unfiltered and filtered samples flagged with a "C" ranged between 21 and 32 µg/L (all results above action level). Samples collected for the RI used trace methods identified in the 100-D/H SAP (DOE/RL-2009-40). All cobalt results (detected concentrations and MDLs) analyzed by trace methods were less than the action level of 4.8 µg/L. Cobalt concentrations above the action level are not associated with a specific location or with a trend. Cobalt results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the action level. However, all cobalt results (detected concentrations and MDLs) analyzed by trace methods are less than the action level. Cobalt concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 0.92 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, cobalt is retained as a COPC for further monitoring.

Copper was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC, and some MDLs were greater than the AWQC of 9.0 µg/L. Copper was detected in 78 of 270 (29 percent) of unfiltered samples and 35 of 255 (14 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater area were compared to the AWQC of 9 µg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640 µg/L. Copper concentrations in unfiltered samples range between 0.12 and 116 μg/L and filtered groundwater samples range between 0.17 and 15 μg/L. All copper results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. MDLs for filtered results reported by Method 6010 range between 2.8 and 70 μg/L (11 of 184 greater than AWQC) and filtered concentrations ranged between 4.4 and 15 µg/L (9 of 16 results greater than AWQC). All but one filtered copper results reported by Method 6010 were flagged with a "B" qualifier (8 of 17 results) or flagged with "C" qualifier (8 of 17 results). Copper concentrations for filtered samples flagged with a "B" ranged between 4.4 and 12.5 µg/L (2 of 8 results above AWQC) and copper concentrations for filtered samples flagged with a "C" ranged between 7.7 and 15.4 µg/L (7 of 8 results above AWQC). Copper was detected in three sample rounds at 199-D5-15 where the highest filtered copper concentrations were reported. Copper concentrations above the AWQC were reported in two of three sampling rounds at this well (all reported by Method 6010). One filtered result was reported during 2010 at 6 μg/L and flagged with a "B" laboratory qualifier and the second filtered result at 199-D5-15 reported during 2007 at 9.6 μg/L and flagged with a "C" qualifier. The remaining round at 199-D5-15 reported copper at a concentrations of 11.6 με/L. Samples collected for the RI were analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40). All copper results for filtered samples (detected concentrations and MDLs) were less than the AWQC. Copper concentrations above the AWQC are not associated with a specific location or with a trend. Some filtered copper results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the AWQC. Copper concentrations associated with samples collected for the RI are less than the AWQC of 9 µg/L. Copper concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 0.81 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, copper is retained as a COPC for further monitoring.

Iron was detected in 137 of 253 (54 percent) of unfiltered and 55 of 255 (22 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater area were compared to the AWQC of 1,000 µg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200 µg/L. All samples were analyzed by Method 6010 as identified in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). All filtered iron results (detected concentrations and MDLs) are less than the AWQC. With the exception of one unfiltered iron result reported at well 199-D5-93, all unfiltered iron concentrations are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Iron was reported at a concentration 11,300 μg/L at well 199-D5-93 in January 2011; however, two previous rounds (843 to 6,420 µg/L) and 10 subsequent rounds (232 to 4,580 µg/L) are reported at concentrations less than the 2007 MTCA groundwater cleanup level. As a result, this iron result does not appear to be associated with an upward trend in iron concentrations. Iron concentrations in filtered water samples are less than the 90<sup>th</sup> percentile Hanford Site background level of 570 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, iron is not retained as a COPC for further evaluation in the FS. Note that although iron is not retained as a COPC for further monitoring in this exposure area, iron is retained as a COPC for further monitoring in the 100-D ISRM exposure area discussed in Section 4.4.1.4 (Table 4-14).

Lead was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standards for surface waters of the state, and some MDLs were greater than the water quality standard of 2.1 µg/L. Lead was detected in 24 of 79 (30 percent) of unfiltered samples and 7 of 58 (12 percent) of filtered groundwater samples. Lead concentrations in unfiltered groundwater samples range between 0.12 and 0.52 µg/L and range between 0.29 and 3.7 µg/L in filtered groundwater samples. Although all monitoring wells within the 100-D Area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 15 µg/L. All lead results (detected concentrations and MDLs) were less than the DWS. All MDLs were less than the state water quality criteria of 2.1 µg/L. Lead in filtered samples was reported above the state water quality standard at two wells (199-D5-142 and 199-D8-101). A single detection of lead was reported at 199-D5-142 (2.24 μg/L) and at 199-D8-101 (3.66 µg/L) and both lead results were flagged with a "B" laboratory qualifier. The "B" qualifier indicates the analyte was detected at a value less than the required detection limit, but greater than or equal to the MDL, indicating that the result is an estimation. Both wells were installed for the RI and are the only results available for these wells. Additionally, samples from these wells were not analyzed by the trace methods identified in the 100-D/H SAP (Method 6020 or 200.8) but were analyzed by Method 6010, which is not accurate for measuring trace levels of lead. Lead concentrations in filtered samples are above the 90th percentile Hanford Site background level of 0.92 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, lead is retained as a COPC for further monitoring. Lead is also retained as a COPC for further monitoring in the 100-D ISRM exposure area discussed in Section 4.4.1.4 (see Table 4-14).

Manganese was detected in 55 of 270 (20 percent) of unfiltered and 30 of 255 (12 percent) of filtered groundwater samples. The action level for manganese of 384  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Manganese concentrations in unfiltered samples range between 0.29 and 814  $\mu$ g/L and filtered groundwater samples range between 3.2 and 28  $\mu$ g/L. Manganese was analyzed a total of 13 rounds between 2011 and 2012 at Well 199-D5-93. During this time frame three of the 13 sample results (435 to 814  $\mu$ g/L) were above the groundwater cleanup level of 384  $\mu$ g/L. These results do not suggest an upward trend in manganese concentrations. Additionally, Well 199-D5-93 was decommissioned because it was located in the

footprint of the 100-D-100 waste site. Manganese concentrations in unfiltered samples are above the  $90^{th}$  percentile Hanford Site background level of 39 µg/L. However, all filtered manganese concentrations are less than the Hanford Site background level. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, manganese is not retained as a COPC for further evaluation in the FS. Note that although manganese is not retained as a COPC for further monitoring in this exposure area, manganese is retained as a COPC for further monitoring in the 100-D ISRM exposure area discussed in Section 4.4.1.4 (see Table 4-14).

Mercury was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC, and some MDLs were greater than the AWQC of 0.012  $\mu$ g/L. The analytical method cannot attain the AWQC; therefore, nondetected concentrations are reported at the EQL of 0.5  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Mercury was not detected in any of the 55 unfiltered groundwater samples (0 percent frequency) and was detected in 3 of 55 (5.4 percent) filtered groundwater samples. All mercury results (detected concentrations and MDLs) were less than the EQL of 0.5  $\mu$ g/L. Mercury concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 0.003  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, mercury is not retained as a COPC for further evaluation in the FS.

Nickel was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC of  $52~\mu g/L$ . Nickel was detected in 86 of 270 (32 percent) unfiltered and 34 of 255 (13 percent) filtered groundwater samples. Nickel concentrations in unfiltered samples range between 0.28 and  $67~\mu g/L$  and filtered groundwater samples range between 0.59 and  $26~\mu g/L$ . Although all monitoring wells within the 100-D Area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of  $100~\mu g/L$ . All nickel results (detected concentrations and MDLs) are less than the DWS. With the exception of four samples analyzed in 2011, all MDLs for filtered samples were less than the AWQC. All detected nickel concentrations in filtered samples are less than the AWQC. Nickel concentrations in filtered samples are above the  $90^{th}$  percentile Hanford Site background level of  $1.6~\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, nickel is not retained as a COPC for further evaluation in the FS.

Selenium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC and some MDLs were greater than the AWQC of 5  $\mu$ g/L. Selenium was detected in 77 of 85 (91 percent) of unfiltered and 65 of 68 (96 percent) of filtered groundwater samples. Selenium concentrations in unfiltered samples range between 0.38 and 10.7  $\mu$ g/L and filtered samples range between 0.44 and 10.5  $\mu$ g/L. With the exception of two samples analyzed in 2011, all samples were analyzed by trace methods identified in the 100-D/H SAP (DOE/RL-2009-40). One filtered sample collected in 2011 after the RI, was reported with an MDL of 10  $\mu$ g/L. All selenium concentrations are less than or equal to the 90<sup>th</sup> percentile Hanford Site background level of 11  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, selenium is not retained as a COPC for further evaluation in the FS.

Silver was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standard (WAC 173-201A), and some MDLs were greater than the standard of 2.6  $\mu$ g/L. The analytical method cannot attain the "Water Quality Standards for Surface Waters of the State of Washington" (WAC 173-201A); therefore, nondetected concentrations are reported at the EQL of 10  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Silver was detected in 22 of 270 (8.2 percent) unfiltered samples and 17 of 255 (6.7 percent) filtered groundwater samples. Although all monitoring wells within the 100-D Area were compared to the state water quality standard, these

standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80 µg/L. All of the unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. Silver concentrations in unfiltered samples range between 0.13 and 34 μg/L and filtered groundwater samples range between 4.6 and 32 µg/L. All detected concentrations are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Twelve of 248 MDLs for unfiltered samples were greater than the 2007 MTCA groundwater cleanup level. A total of 69 of 238 MDLs for filtered samples were greater than the EQL. Eleven of 17 silver detections from filtered samples were greater than the EQL. All but one silver detection from filtered sample results reported by Method 6010 were flagged with a "B" qualifier, flagged with "C" qualifier, or flagged with both a "B" and a "C" qualifier. Silver concentrations for filtered samples flagged with a "B" ranged between 4.6 and 20 µg/L. Silver concentrations for filtered samples flagged with a "C" or "BC" ranged between 6.5 and 32 µg/L. All historical detections of silver are flagged with a combination of "B" and "C" qualifiers indicating they are estimated concentrations or are the result of laboratory contamination. Silver concentrations are not associated with a specific location or a trend and silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the state water quality standard or the EQL. Silver concentrations associated with samples collected for the RI are not above 2.6 μg/L and are also below the 90th percentile Hanford Site background level of 5.3 μg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, silver is retained as a COPC for further monitoring.

Thallium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS goal and some MDLs were greater than the DWS goal of 0.5  $\mu$ g/L. The analytical method cannot attain the DWS goal of 0.5  $\mu$ g/L; therefore, nondetected concentrations are reported at the EQL of 2  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). All but one sample were analyzed by trace methods identified in the 100-D/H SAP (DOE/RL-2009-40). Thallium was detected in 3 of 73 (4.1 percent) unfiltered samples and 4 of 56 (7.1 percent) of filtered groundwater samples. Two samples were analyzed by Method 6010 and the nondetected concentrations were reported at 5  $\mu$ g/L. Except for these two samples analyzed in 2011 by Method 6010, all thallium results (detected concentrations and MDLs) are less than the EQL of 2  $\mu$ g/L, and thallium concentrations in unfiltered and filtered samples are below the 90<sup>th</sup> percentile Hanford Site background level of 1.7  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, thallium is not retained as a COPC for further evaluation in the FS.

Uranium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of 30  $\mu$ g/L. Uranium was detected in all unfiltered groundwater samples (129 samples) and all filtered groundwater samples (18 samples). All uranium results (detected concentrations and MDLs) were less than the DWS of 30  $\mu$ g/L. Uranium concentrations in unfiltered and filtered samples are below the 90<sup>th</sup> percentile Hanford Site background level of 9.9  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, uranium is not retained as a COPC for further evaluation in the FS.

Vanadium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level of 80  $\mu$ g/L. The action level for vanadium of 80  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Vanadium was detected in 151 of 270 (56 percent) unfiltered samples and 114 of 255 (45 percent) of filtered groundwater samples. Samples collected for purposes other than the RI reported MDLs that range between 4.1 and 140  $\mu$ g/L (21 samples collected in 2006 report MDLs equal to 140  $\mu$ g/L). Samples collected for the RI reported MDLs that ranged between 4.1 and 12  $\mu$ g/L. All detected vanadium concentrations are less than the action level of 80  $\mu$ g/L. Vanadium concentrations in filtered samples are

above the  $90^{th}$  percentile Hanford Site background level of  $12~\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standard (WAC 173-201A) and some MDLs were greater than the state water quality standard of 91 µg/L. Zinc was detected in 123 of 270 (46 percent) unfiltered samples and 91 of 255 (36 percent) filtered groundwater samples. All samples were analyzed by Method 6010 as identified in the 100-D/H SAP (DOE/RL-2009-40). Although all monitoring wells within the 100-D Area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 µg/L. All zinc results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 µg/L. MDLs for filtered samples analyzed by Method 6010 ranged between 4 and 20 µg/L and detected concentrations for filtered samples ranged between 4.0 and 260 µg/L. Some zinc results reported by Method 6010 were flagged with a "B" qualifier (26 of 44 results), with a "C" qualifier (9 of 44 results), or with both a "B" and a "C" qualifier (1 of 44 results). Zinc concentrations in filtered samples flagged with a "B" ranged between 4.0 and 41 µg/L (all less than the state water quality standard). Zinc concentrations in filtered samples flagged with a "C" or with a "BC" ranged between 10 and 154 μg/L (one of 10 results greater than the state water quality standard). A single occurrence of zinc at concentrations greater than the water quality standard was reported in filtered samples at six wells including 199-D2-6, 199-D5-15, 199-D5-36, 199-D5-38, 199-D5-40, and 199-D5-44. Zinc concentrations at these six wells ranged between 96 and 215 μg/L and each sample was collected between November 14, 2006, and December 7, 2006. Between four and eight additional sample rounds at these locations reported zinc at concentrations less than the water quality standard. Similar results are observed in well 199-D4-15 as zinc was reported at a concentration of 260 μg/L on November 20, 2006; zinc was reported above the water quality standard in two subsequent sample rounds. However, the zinc result for the sample collected on November 12, 2006 was flagged with a "C" qualifier and the sample collected on September 27, 2012 slightly exceeded the standard (101 µg/L). These results suggest that zinc was potentially introduced in the laboratory after the sample was collected in the field between November and December 2006 and is the result of laboratory contamination in well 199-D4-15 in November 2007. With the exception of the above wells, zinc concentrations are less than the water quality standard. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, zinc is not retained as a COPC for further evaluation in the FS. Note that although zinc is not retained as a COPC for further monitoring in this exposure area, zinc is retained as a COPC for further monitoring in the 100-D ISRM exposure area discussed in Section 4.4.1.4 (see Table 4-14).

Summary of the 100-D Groundwater Area Groundwater Evaluation. Table 4-9 summarizes the outcome of the analysis. Contaminants that warrant further evaluation in the FS are chromium (total), Cr(VI), nitrate, and strontium-90. Groundwater contaminants that do not warrant further evaluation in the FS, because they have infrequent detections above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency.

Table 4-9. Summary of 100-D Groundwater Area Contaminant Evaluation

Category	Constituent
Retained as	a COPC
Contaminant of potential concern* (contaminants that warrant further evaluation in FS)	Chromium, Cr(VI), nitrate, strontium-90
Retained for I	Monitoring
Detected at levels above action level and background	Antimony, cadmium, chloroform, cobalt, copper, lead, silver
Not Retained	as a COPC
Detected in groundwater but below action level, EQL, or background concentrations	Arsenic, beryllium, carbon tetrachloride, fluoride, gross alpha, iron, manganese, mercury, nickel, nitrite, selenium, sulfate, technetium-99, thallium, tritium, uranium, vanadium, zinc
Not detected in groundwater	1,1-Dichloroethene, benzene, cesium-137, cobalt-60, europium-152. europium-154, europium-155, trichloroethene, vinyl chloride

<sup>\*</sup> Based on evaluation of data collected January 2006 through December 2012.

COPC = contaminant of potential concern

EQL = estimated quantitation limit

FS = feasibility study

### Historical COPCs—100-H Groundwater Area

The following subsections describe historical COPCs that were detected at least once in the 100-H groundwater area and include radionuclides, VOCs, anions, and metals. As described earlier, historical COPCs are either those analytes that were identified as COPCs in the 100-D/H SAP (DOE/RL-2009-40), or those analytes for which a maximum concentration exceeding an action level was reported during the spatial and temporal sampling (Section 6.3). Summary statistics for groundwater within the 100-H Area are shown in Appendix N (Table N-2).

Radionuclides. Gross alpha and gross beta were identified as additional analytes in the 100-D/H SAP (DOE/RL-2009-40). Gross alpha and gross beta were analyzed in all of the RI monitoring network wells during all sampling rounds, as well as in the in the larger populations of wells over the longer period. Gross alpha was detected in 31 percent of the unfiltered groundwater samples and gross beta was detected in 94 percent of the unfiltered samples. Gross alpha was detected at concentrations ranging between 1.2 and 51 pCi/L. Gross alpha was measured above the DWS of 15 pCi/L at well 199-H4-84 during July 2012 (16 pCi/L) and August 2012 (51 pCi/L). Gross beta was detected at concentrations ranging between 3.5 and 330 pCi/L; gross beta concentrations are consistent with the presence of tritium and strontium-90. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, gross alpha and gross beta are not retained as COPCs for further evaluation in the FS.

Technetium-99 was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of 900 pCi/L. Technetium-99 was detected in 47 of 171 (27 percent) of the unfiltered groundwater samples with concentrations ranging between 6.5 and 870 pCi/L. The results of this evaluation indicate that technetium-99 has been historically detected at

concentrations less than the DWS of 900 pCi/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, technetium-99 is not retained as a COPC for further evaluation in the FS.

Tritium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of 20,000 pCi/L. Tritium was detected in 201 of 210 (96 percent) of the unfiltered groundwater samples with concentrations ranging between 7.3 and 11,000 pCi/L. The results of this evaluation indicate that tritium has been historically detected at concentrations less than the DWS of 20,000 pCi/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, tritium is not retained as a COPC for further evaluation in the FS.

Volatile Organic Compounds. Carbon tetrachloride was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for carbon tetrachloride of 0.63 µg/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The analytical method cannot attain the action level for carbon tetrachloride; therefore, nondetected concentrations are reported at the EQL of 1 µg/L identified in the 100-D/H SAP (DOE/RL-2009-40). Carbon tetrachloride was detected in 3 of 57 unfiltered groundwater samples (5.3 percent) at concentrations ranging between 0.088 and 2 µg/L. Carbon tetrachloride was detected once in 199-H4-10 (0.088 µg/L) at a concentration less than the EQL of 1 µg/L. Carbon tetrachloride was analyzed at 199-H4-10 in one previous and one subsequent sampling round and reported with nondetected concentrations less than or equal to the EQL. Carbon tetrachloride was detected once in 199-H4-11 (2 μg/L) at a concentration greater than the EQL of 1 μg/L. Carbon tetrachloride was analyzed in two subsequent sampling rounds at 199-H4-11 and reported at nondetected concentrations less than the EQL. Carbon tetrachloride was detected in well 199-H3-5 (1.2 µg/L) at a concentration greater than the EQL of 1 μg/L. Carbon tetrachloride was analyzed at 199-H3-5 in five previous and one subsequent sampling round and reported with nondetected concentrations less than or equal to the EQL. All MDLs are less than or equal to the EQL listed in the 100-D/H SAP (DOE/RL-2009-40). The presence of carbon tetrachloride in these three wells does not suggest it is associated with a trend. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, carbon tetrachloride is not retained as a COPC for further evaluation in the FS.

Chloroform was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for chloroform of 1.4  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The analytical method cannot attain the action level for chloroform; therefore, nondetected concentrations are reported at the EQL of 5  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Chloroform was detected in 39 of 57 (68 percent) of unfiltered groundwater samples with concentrations ranging between 0.32  $\mu$ g/L and 2  $\mu$ g/L. All results (detected concentrations and MDLs) are less than the EQL of 5  $\mu$ g/L. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, chloroform is not retained as a COPC for further evaluation in the FS.

**Anions.** Fluoride was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and some MDLs were greater than the action level of 960  $\mu$ g/L. The action level of 960  $\mu$ g/L for fluoride is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Fluoride was detected in 184 of 248 (74 percent) of unfiltered groundwater samples, with concentrations ranging between 49  $\mu$ g/L and 308  $\mu$ g/L. All fluoride results (detected concentrations and MDLs) are less than the action level. Fluoride

concentrations in unfiltered samples are also less than the  $90^{th}$  percentile Hanford Site background level of 1,047 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, fluoride is not retained as a COPC for further evaluation in the FS.

Nitrite was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS, and some MDLs were greater than the DWS of 3,300  $\mu$ g/L. Nitrite was detected in 62 of 241 (26 percent) of unfiltered samples with concentrations ranging between 9.9 and 296  $\mu$ g/L. All nitrite results (detected concentrations and MDLs) were less than the DWS of 3,300  $\mu$ g/L. Nitrite concentrations in unfiltered samples are greater than the 90<sup>th</sup> percentile Hanford Site background level of 94  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, nitrite is not retained as a COPC for further evaluation in the FS.

Sulfate was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the secondary DWS of 250,000  $\mu g/L$ . Sulfate was detected in 100 percent of unfiltered groundwater samples (248 samples) with concentrations ranging between 10,200 and 149,000  $\mu g/L$ . All sulfate results are less than the secondary DWS of 250,000  $\mu g/L$ . Sulfate concentrations in unfiltered samples are greater than the 90<sup>th</sup> percentile Hanford Site background level of 47,000  $\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, sulfate is not retained as a COPC for further evaluation in the FS.

Metals. Antimony was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for antimony is 6 µg/L based on the DWS. Antimony was detected in 16 of 197 unfiltered samples (8.1 percent) and 11 of 193 (5.7 percent) of the filtered groundwater samples. Antimony concentrations in unfiltered and filtered groundwater samples ranged between 0.34 and 49 μg/L. Most unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. MDLs for results reported by Method 6010 range between 4 and 72 μg/L (261 of 268 greater than DWS) and detected concentrations range between 36 and 49 µg/L (all 7 greater than the DWS). Two of seven antimony detected results reported by Method 6010 were flagged with a "B" laboratory qualifier. For samples analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs ranged between 0.3 and 0.6 µg/L and the detected concentrations range between 0.34 and 1.0 µg/L. The results of this evaluation indicate that antimony has historically been detected in groundwater samples at a low frequency of detection (8.1 percent in unfiltered samples and 5.7 percent in filtered samples) with concentrations more than 7.5 times greater than the standard. Some historical detections of antimony are flagged with a "B" qualifier. Antimony concentrations are not associated with a specific location or a trend and antimony results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the action level. Antimony concentrations reported by methods identified in the 100-D/H SAP (DOE/RL-2009-40) are below the action of 6 µg/L. All detected antimony concentrations are below the 90<sup>th</sup> percentile Hanford Site background level of 55 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, antimony is retained as a COPC for further monitoring.

Arsenic was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and all MDLs were greater than the action level. The action level for arsenic of 0.058  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. However, the analytical method cannot attain the action level; therefore, nondetected concentrations are reported at the EQL of 4  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Arsenic was detected in 61 of 62 (98 percent) of the unfiltered and 51 of 53 (96 percent) of the filtered groundwater samples. Arsenic concentrations range between 1.3 and 4.0  $\mu$ g/L in unfiltered and filtered groundwater samples. Minimum, maximum, and 90<sup>th</sup> percentile concentrations for

(filtered) background concentrations of arsenic are 0.5, 8.8, and 7.85  $\mu$ g/L, respectively. All arsenic concentrations in unfiltered and filtered samples are less than the 90<sup>th</sup> percentile Hanford Site background concentration. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, arsenic is not retained as a COPC for further evaluation in the FS.

Beryllium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS, and most MDLs were greater than the DWS of 4  $\mu$ g/L. Beryllium was detected in 1 of 191 (0.52 percent) of the unfiltered samples and in 5 of 193 (2.6 percent) of the filtered groundwater samples. Beryllium concentrations in unfiltered and filtered groundwater samples range between 0.072 and 0.63  $\mu$ g/L. All beryllium results (detected concentrations and MDLs) are less than the DWS of 4  $\mu$ g/L. In addition, all beryllium concentrations are less than the 90<sup>th</sup> percentile Hanford Site background level of 2.3  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC, and most MDLs were greater than the AWQC of 0.25 µg/L. Although all monitoring wells within the groundwater 100-H Area were compared to the AWQC of 0.25 μg/L, only these standards only apply for groundwater where it enters the Columbia River wells would need to meet this criterion. Wells located inland would need to meet the DWS of 5 µg/L. Cadmium was detected in 1 of 197 (0.51 percent) of the unfiltered samples and in 1 of 193 (0.52 percent) of the filtered groundwater samples. All cadmium results (detected concentration and MDLs) were less than the DWS. Most filtered samples collected for purposes other than the RI were analyzed by Method 6010. MDLs for filtered results reported by Method 6010 range between 0.86 and 4.1 μg/L(all greater than the AWQC) and no detected concentrations were reported. For samples analyzed using the trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs range between 0.1 and 0.2 μg/L (all less than the AWOC). Cadmium was detected above the AWOC in one well (199-H4-13). Cadmium concentrations above the AWQC in filtered samples were reported in one of 13 sample rounds conducted at 199-H4-13; the filtered sample (0.39 µg/L) was flagged with a "B" qualifier and eight previous rounds and four subsequent rounds were reported as not detected concentrations less than the AWQC. The results of this evaluation indicate that cadmium has historically been detected in groundwater samples at a low frequency (less than one percent in unfiltered and filtered samples). Cadmium concentrations in unfiltered and filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 0.92 μg/L. The single filtered cadmium detection above the AWOC does not appear to be associated with a trend. Additionally, cadmium MDLs reported by Method 6010 are not accurate at concentrations at or near the AWQC. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, cadmium is retained as a COPC for further monitoring.

Chromium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC of 65  $\mu$ /L. Chromium was detected in 158 of 197 (80 percent) of unfiltered samples and 131 of 193 (68 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. Chromium concentrations in unfiltered samples range between 1.4 and 215  $\mu$ g/L and filtered samples range between 4.9 and 79  $\mu$ g/L. Chromium concentrations in unfiltered samples above the DWS were reported at well 199-H4-18 (215  $\mu$ g/L) and well 199-H4-9 (101  $\mu$ g/L). Chromium was analyzed twice at 199-H4-18; chromium was reported at a concentration of 215  $\mu$ g/L in October 2009 and at 36  $\mu$ g/L in November 2009. Chromium was analyzed 13 times at Well 199-H4-9 between 2006 and 2012; chromium was reported above the DWS once in 2011 (101  $\mu$ g/L). Chromium concentrations in filtered samples above the AWQC of 65  $\mu$ g/L were reported at 199-H3-4 and 199-H3-5. Filtered chromium concentrations above the AWQC were reported in one of three sample rounds at 199-H3-4 (concentrations range between 52

and  $66 \mu g/L$ ). Filtered chromium concentrations above the AWQC were reported in all four samples at 199-H3-5, with concentrations ranging between 71 and 79  $\mu g/L$ . Filtered chromium concentrations at 199-H3-5 appear to be associated with a trend. Chromium concentrations in filtered and unfiltered samples are greater than the  $90^{th}$  percentile Hanford Site background level of 2.4  $\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, chromium is retained as a COPC for further evaluation in the FS.

Cobalt was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and some MDLs were greater than the action level. The action level for cobalt of 4.8 µg/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Cobalt was detected in 28 of 196 (15 percent) unfiltered samples and 36 of 193 (19 percent) filtered groundwater samples. Cobalt concentrations in unfiltered and filtered groundwater samples range between 0.062 and 29 µg/L. Unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. The MDLs for results reported by Method 6010 range between 1.4 and 7 μg/L (33 of 265 greater than action level), unfiltered concentrations ranged between 4.1 and 27 µg/L (2 of 3 results greater than action level), and filtered concentrations ranged between 4.3 and 29 µg/L (6 of 8 results greater than action level). Most cobalt results (9 of 11) reported by Method 6010 were flagged with a "B" qualifier or flagged with "C" qualifier. Cobalt concentrations for unfiltered and filtered samples flagged with a "B" ranged between 4.1 and 7.9 µg/L (two of five results above action level). Cobalt concentrations for unfiltered and filtered samples flagged with a "C" ranged between 25 and 29 µg/L (all results above action level). For samples analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs ranged between 0.05 and 0.1 µg/L, detected concentrations for unfiltered samples ranged between 0.062 and 0.9 µg/L, and concentrations ranged between 0.083 and 2.8 µg/L for filtered samples. Cobalt concentrations above the action level are not associated with a specific location or with a trend. Cobalt results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the action level. However, all cobalt results (detected concentrations and MDLs) analyzed by trace methods are less than the action level. Cobalt concentrations in filtered samples are above the 90th percentile Hanford Site background level of 0.92 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, cobalt is retained as a COPC for further monitoring.

Copper was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWOC, and some MDLs were greater than the AWOC of 9.0 µg/L. Copper was detected in 55 of 197 (28 percent) unfiltered samples and 20 of 193 (10 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater 100-H Area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640 µg/L. Copper concentrations in unfiltered samples range between 0.12 and 28 µg/L and filtered groundwater samples range between 0.17 and 13 µg/L. All copper results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Filtered samples collected for purposes other than the RI were analyzed by Method 6010. MDLs for filtered results reported by Method 6010 ranged between 2.8 and 10 µg/L (3 of 136 greater than AWQC) and filtered concentrations ranged between 2.9 and 13 µg/L (2 of 9 greater than the AWQC). Seven of nine filtered copper results reported by Method 6010 were flagged with a "B" qualifier, flagged with "C" qualifier, or flagged with a "BC" qualifier. Copper concentrations for filtered samples flagged with a "B" ranged between 2.9 and 6 ug/L (no results above AWQC). Copper concentrations for filtered samples flagged with a "C" or a "BC" ranged between 4.2 and 13 μg/L (3 of 5 results above AWQC). For samples analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs range between 0.1 and 0.2 µg/L and

detected concentrations in filtered samples ranged between 0.16 and 1.6  $\mu g/L$ . Copper results concentrations above the AWQC that are reported by Method 6010 are not associated with a specific location or with a trend. Copper results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the AWQC. All copper concentrations associated with samples collected for the RI are less than the AWQC of 9  $\mu g/L$ . Copper concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 0.81  $\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, copper is retained as a COPC for further monitoring.

Iron was detected in 135 of 180 (75 percent) of unfiltered and 93 of 193 (48 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater 100-H Area were compared to the AWQC of 1,000  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200  $\mu$ g/L. All samples were analyzed by Method 6010 as identified in the 100-D/H SAP (DOE/RL-2009-40). Iron concentrations in unfiltered samples range between 10 and 7,840  $\mu$ g/L and range between 9.5 and 426  $\mu$ g/L in filtered samples. All unfiltered iron results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All filtered iron results (detected concentrations and MDLs) are less than the AWQC. Iron concentrations in filtered water samples are less than the background level of 570  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, iron is not retained as a COPC for further evaluation in the FS.

Lead was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and some MDLs were greater than the action level of 2.1 µg/L. Lead was detected in 14 of 63 (22 percent) unfiltered and 6 of 50 (12 percent) filtered groundwater samples. Lead concentrations in unfiltered samples range between 0.093 and 0.71 µg/L and filtered groundwater samples range between 0.21 and 2.5 µg/L. Although all monitoring wells within the 100-H Area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River of 2.1 µg/L. Wells located inland would need to meet the DWS of 15 µg/L. All lead results (detected concentrations and MDLs) were less than the DWS. Except for three filtered results collected for purposes other than the R1, all samples were analyzed by trace methods identified in the 100-D/H SAP (DOE/RL-2009-40). All lead results (detected concentrations and MDLs) for the trace methods were less than the state water quality standard of  $2.1 \mu g/L$  whereas the MDLs reported by Method 6010 were  $3.1 \mu g/L$ and 10 µg/L. Lead results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the state water quality standard. Lead concentrations in unfiltered and all but one filtered result are less than the 90<sup>th</sup> percentile Hanford Site background level of 0.92 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, lead is retained as a COPC for further monitoring.

Manganese was detected in 52 of 197 (26 percent) of unfiltered and 39 of 193 samples (20 percent) of filtered groundwater samples. The action level for manganese of 384  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Manganese concentrations in unfiltered samples range between 0.28 and 340 and filtered groundwater samples range between 0.8 and 229  $\mu$ g/L. All manganese results (detected concentrations and MDLs) were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 384  $\mu$ g/L. Manganese concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 39  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, manganese is not retained as a COPC for further evaluation in the FS.

Mercury was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC, and some MDLs were greater than the AWQC of  $0.012~\mu g/L$ . The analytical method for mercury cannot attain the AWQC; therefore, nondetected concentrations are reported at the EQL of  $0.5~\mu g/L$  identified in the 100-D/H SAP (DOE/RL-2009-40). Mercury was detected in 1 of 47 (2.1 percent) unfiltered samples and 1 of 46 (2.2 percent) of the filtered groundwater samples. All mercury results (detected concentrations and MDLs) are less than the EQL of  $0.5~\mu g/L$ . Mercury concentrations in one filtered sample are above the  $90^{th}$  percentile Hanford Site background level of  $0.003~\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, mercury is not retained as a COPC for further evaluation in the FS.

Nickel was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC of 52  $\mu$ g/L. Nickel was detected in 82 of 197 (42 percent) unfiltered samples and 49 of 193 (25 percent) filtered groundwater samples. Although all monitoring wells within the area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. Nickel concentrations in unfiltered samples range between 0.23 and 37  $\mu$ g/L and filtered groundwater samples range between 0.72 and 36  $\mu$ g/L. All nickel results (detected concentrations and MDLs) are less than the DWS. All detected nickel concentrations in filtered samples are less than the AWQC however, two MDLs for filtered samples (66.5  $\mu$ g/L) were greater than the AWQC. All samples were analyzed by Method 6010 as identified in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). All detected concentrations and all but two MDLs were less than the AWQC. Nickel concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 1.6  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, nickel is not retained as a COPC for further evaluation in the FS.

Selenium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC, and some MDLs were greater than the AWQC of 5  $\mu$ g/L. Selenium was detected in 49 of 62 (79 percent) unfiltered samples and 48 of 52 (92 percent) filtered groundwater samples. Although all monitoring wells within the 100-H Area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 50  $\mu$ g/L. All selenium results (both detected concentrations and MDLs) are less than the AWQC and the DWS. All selenium concentrations and MDLs are less than the AWQC. All selenium concentrations are less than the 90<sup>th</sup> percentile Hanford Site background level of 11  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, selenium is not retained as a COPC for further evaluation in the FS.

Silver was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standard (WAC 173-201A), and some MDLs were greater than the standard of 2.6  $\mu$ g/L. The analytical method cannot attain the "Water Quality Standards for Surface Waters of the State of Washington" (WAC 173-201A); therefore, nondetected concentrations are reported at the EQL of 10  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Silver was detected in 9 of 197 (4.6 percent) unfiltered and 6 of 193 (3.1 percent) filtered groundwater samples. Although all monitoring wells within the 100-H Area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Silver concentrations in unfiltered samples range between 6.1 and 30  $\mu$ g/L and filtered groundwater samples ranged between 0.32 and 33  $\mu$ g/L. All silver results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Most of the unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. MDLs for filtered samples analyzed by method 6010 ranged between 2.2 and 11  $\mu$ g/L (139 of 140 greater than state standard) and detected concentrations

ranged between 7.8 and 33  $\mu$ g/L (all results greater than state standard). Silver results for all samples reported by Method 6010 were flagged with a "B" qualifier or flagged with "C" qualifier. Silver results flagged with a "B" ranged between 6.2 and 14  $\mu$ g/L. Silver concentrations for unfiltered and filtered samples flagged with a "C" ranged between 6.1 and 33  $\mu$ g/L. The samples collected for the RI were analyzed by trace methods, although Method 6010 is identified in the 100-D/H SAP (DOE/RL-2009-40). MDLs for filtered samples range between 0.05 and 0.2  $\mu$ g/L and the single detected concentrations in a filtered sample was 0.32  $\mu$ g/L. All but one detection of silver in filtered samples are flagged with either a of "B" or "C" qualifier. Silver concentrations above the state water quality standard are not associated with a specific location or a trend and silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the standard. Silver concentrations associated with samples collected for the RI are not above the standard of 2.6  $\mu$ g/L and are also below the 90<sup>th</sup> percentile Hanford Site background level of 5.3  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, silver is retained as a COPC for further monitoring.

Thallium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS goal and some MDLs were greater than the DWS goal of 0.5  $\mu$ g/L. The analytical method cannot attain the DWS goal of 0.5  $\mu$ /L; therefore, nondetected concentrations are reported at the EQL of 2  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Thallium was detected in 2 of 58 (3.4 percent) of unfiltered and 3 of 48 (6.2 percent) of filtered groundwater samples. All detected concentrations are less than the EQL of 2  $\mu$ g/L. All but four samples report MDLs less than the EQL of 2  $\mu$ g/L. These four samples were analyzed by Method 6010 and their associated MDLs range between 5 and 7  $\mu$ g/L. All detected thallium concentrations in unfiltered and filtered samples are below the 90<sup>th</sup> percentile Hanford Site background level of 1.7  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, thallium is not retained as a COPC for further evaluation in the FS.

Uranium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of  $30~\mu\text{g/L}$ . Uranium was detected in 168~of~171~(98~percent) unfiltered samples and all 27 of the filtered groundwater samples. Uranium concentrations range between  $0.38~\text{and}~86~\mu\text{g/L}$  in unfiltered groundwater samples and between  $0.42~\text{and}~13~\mu\text{g/L}$  in filtered groundwater samples. All MDLs were less than the DWS of  $30~\mu\text{g/L}$ . Uranium was reported above the DWS in an unfiltered sample collected at  $199\text{-H4-3}~(86~\mu\text{g/L})$  during May 2006. Uranium concentrations fell below the DWS from November 2006~through December  $2010~\text{(concentrations ranged between }6.7~\text{and}~14~\mu\text{g/L})$ . During October 2011~and October 2012, uranium concentrations increased to levels near or above the DWS ( $29~\text{and}~37~\mu\text{g/L}$ ). Subsequently, uranium concentrations decreased to  $17~\mu\text{g/L}$  in February 2014. Well 199-H4-3 monitors groundwater conditions near the 183-H Solar Evaporation Basin. Uranium concentrations in unfiltered and filtered samples are greater than the  $90^{\text{th}}$  percentile Hanford Site background level of  $9.9~\mu\text{g/L}$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, uranium is retained as a COPC for further monitoring.

Vanadium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level of 80  $\mu$ g/L. The action level for vanadium of 80  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Vanadium was detected in 63 of 197 (32 percent) unfiltered and 44 of 193 (23 percent) filtered groundwater samples. All vanadium results (detected concentrations and MDLs) are less than the action level of 80  $\mu$ g/L. Vanadium concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford (Site background level of 12  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standard (WAC 173-201A), and some MDLs were greater than the standard of 91 μg/L. Zinc was detected in 56 of 197 (28 percent) unfiltered and 32 of 193 (17 percent) filtered groundwater samples. All samples were analyzed by Method 6010 as identified in the 100-D/H SAP (DOE/RL-2009-40). Although all monitoring wells within the area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 μg/L. All zinc results (detected concentrations and MDLs) were less than the 2007 MTCA groundwater cleanup level. All filtered zinc results (detected concentrations and MDLs) were less than the state water quality standard. Zinc concentrations are greater than the 90<sup>th</sup> percentile Hanford Site background level of 22 μg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, zinc is not retained as a COPC for further evaluation in the FS.

Summary of the 100-H Groundwater Area Groundwater Evaluation. Table 4-10 summarizes the outcome of the analysis. Contaminants that warrant further evaluation in the FS are chromium (total), Cr(VI), nitrate, and strontium-90. Groundwater contaminants that do not warrant further evaluation in the FS, but have infrequent detections above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency.

Table 4-10. Summary of 100-H Groundwater Area Contaminant Evaluation

Category	Constituent
Retained as	a COPC
Contaminant of potential concern* (contaminants that warrant further evaluation in FS)	Chromium, Cr(VI), nitrate, strontium-90
Retained for I	Monitoring
Detected at levels above action level and background	Antimony, cadmium, cobalt, copper, lead, silver, uranium
Not Retained	as a COPC
Detected in groundwater but below action level, EQL, or background concentrations	Arsenic, beryllium, carbon tetrachloride, chloroform, fluoride, gross alpha, gross beta, iron, manganese, mercury, nickel, nitrite, selenium, sulfate, technetium-99, thallium, tritium, vanadium, zinc
Not detected in groundwater	1,1-Dichloroethene, benzene, cesium-137, cobalt-60, europium-152. europium-154, europium-155, trichloroethene, vinyl chloride

<sup>\*</sup> Based on evaluation of data collected January 2006 through December 2012.

COPC = contaminant of potential concern

EQL = estimated quantitation limit

FS = feasibility study

# Historical COPCs—Horn Groundwater Area

The following subsections describe the analytes of interest that were detected at least once in the Horn groundwater area and include radionuclides, VOCs, anions, and metals. As described earlier, analytes of

interest are either those analytes that were identified as COPCs in the 100-D/H SAP (DOE/RL-2009-40) or those analytes for which a maximum concentration exceeding an action level was reported during the spatial and temporal sampling (Section 6.3). Summary statistics for groundwater within the Horn area are shown in Appendix N, Table N-3.

**Radionuclides.** Gross alpha and gross beta were identified as additional analytes in the 100-D/H SAP (DOE/RL-2009-40). Gross alpha and gross beta were analyzed in all of the RI monitoring network wells during all sampling rounds, as well as in the larger populations of wells over the longer period. Gross alpha was detected in 26 percent of the unfiltered groundwater samples and gross beta was detected in 77 percent of the unfiltered samples. Gross alpha was detected at concentrations ranging between 1.4 and 14 pCi/L, which is less than the DWS of 15 pCi/L. Gross beta was detected at concentrations ranging between 2.4 and 21 pCi/L; gross beta concentrations are consistent with the presence of tritium. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, gross alpha and gross beta are not retained as COPCs for further evaluation in the FS.

Strontium-90 was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS. Strontium-90 was detected in 2 of 58 (3.4 percent) of the unfiltered groundwater samples with concentrations of 2.4 and 4.2 pCi/L. All strontium-90 results (detected concentrations and MDLs) were all less than the DWS of 8 pCi/L. The results of this evaluation and the groundwater risk assessment presented in Section 6.3, strontium-90 is not retained as a COPC for further evaluation in the FS.

Technetium-99 was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS. Technetium-99 was detected in 1 of 55 (1.8 percent) of the unfiltered groundwater samples at a concentration of 12 pCi/L. All technetium-99 results (detected concentrations and MDLs) are less than the DWS of 900 pCi/L. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, technetium-99 is not retained as a COPC for further evaluation in the FS.

Tritium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS. Tritium was detected in 197 of 207 (95 percent) of the unfiltered groundwater samples with concentrations ranging between 200 and 6,030 pCi/L. All tritium results (detected concentrations and MDLs) are less than then DWS of 20,000 pCi/L. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, tritium is not retained as a COPC for further evaluation in the FS.

### Volatile Organic Compounds.

Carbon tetrachloride was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for carbon tetrachloride of 0.63  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The analytical method cannot attain the action level for carbon tetrachloride; therefore, nondetected concentrations are reported at an EQL of 1  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Carbon tetrachloride was detected in 10 of 78 unfiltered groundwater samples (13 percent) at concentrations ranging between 0.16 and 1.7  $\mu$ g/L. Carbon tetrachloride was detected in 2009 once at well 699-94-43 (1.4 J  $\mu$ g/L), 699-95-48 (1.5 J  $\mu$ g/L), 699-95-51 (1.3 J  $\mu$ g/L), 699-96-52B (1.3 J  $\mu$ g/L), 699-97-41 (1.1 J  $\mu$ g/L), 699-97-48B (1.1 J  $\mu$ g/L), 699-98-43 (1.0 J  $\mu$ g/L), and 699-98-49A (1.7 J  $\mu$ g/L) at concentrations slightly greater than or equal to the EQL of 1  $\mu$ g/L. Four to five subsequent sampling rounds were conducted at 699-97-41, 699-94-43, 699-95-48, 699-95-51, 699-96-52B, 699-97-48B, 699-98-43, and 699-98-49A, each reporting nondetected concentrations with MDLs less than or equal to the EQL. Carbon tetrachloride was detected twice in 699-95-45 (1.4  $\mu$ g/L and 0.16  $\mu$ g/L)

at concentrations greater than and less than the EQL of 1  $\mu$ g/L. Three subsequent sampling rounds were reported with nondetected concentrations less than or equal to the EQL. All MDLs are less than or equal to the EQL listed in the 100-D/H SAP (DOE/RL-2009-40). The infrequent presence of carbon tetrachloride above the EQL does not suggest it is associated with a specific location or a trend. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, carbon tetrachloride is retained as a COPC for further monitoring.

Chloroform was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for chloroform of 1.4  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The analytical method cannot attain the action level for chloroform; therefore, nondetected concentrations are reported at the EQL of 5  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Chloroform was detected in 33 of 78 (42 percent) unfiltered groundwater samples at concentrations ranging between 0.16 and 1  $\mu$ g/L. All results (detected concentrations and MDLs) are less than the EQL of 5  $\mu$ g/L. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, chloroform is not retained as a COPC for further evaluation in the FS.

Trichloroethene was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for trichloroethene of 0.95 µg/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The analytical method cannot attain the action level; therefore, nondetected concentrations are reported at the EQL of 1 µg/L identified in the 100-D/H SAP (DOE/RL-2009-40). Trichloroethene was detected in 3 of 78 (3.9 percent) unfiltered groundwater samples. All results (detected concentrations and MDLs) are less than or equal to the EQL listed in the 100-D/H SAP (DOE/RL-2009-40). Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, trichloroethene is not retained as a COPC for further evaluation in the FS.

**Anions.** Fluoride was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and some MDLs were greater than the action level of 960  $\mu$ g/L. The action level of 960  $\mu$ g/L for fluoride is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Fluoride was detected in 177 of 226 (78 percent) of unfiltered groundwater samples. All results (detected concentrations and MDLs) were less than the action level of 960  $\mu$ g/L. Fluoride concentrations in unfiltered samples are also less than the 90<sup>th</sup> percentile Hanford Site background level of 1,047  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, fluoride is not retained as a COPC for further evaluation in the FS.

Nitrate was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of  $45,000~\mu g/L$ . Nitrate was detected in all unfiltered groundwater samples (226 samples). All results (detected concentrations and MDLs) were less than the DWS of  $45,000~\mu g/L$ . Nitrate concentrations in unfiltered samples are greater than the  $90^{th}$  percentile Hanford Site background level of  $26,900~\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, nitrate is not retained as a COPC for further evaluation in the FS.

Nitrite was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS, and some MDLs were greater than the DWS of 3,300  $\mu$ g/L. Nitrite was detected in 31 of 224 (14 percent) of unfiltered samples. All results (detected concentrations and MDLs) were less than the DWS of 3,300  $\mu$ g/L. Nitrite concentrations in unfiltered samples are

greater than the  $90^{th}$  percentile Hanford Site background level of 94  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, nitrite is not retained as a COPC for further evaluation in the FS.

Sulfate was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the secondary DWS of  $250,000~\mu\text{g/L}$ . Sulfate was detected in 100~percent of unfiltered samples (226~samples). All results (detected concentrations and MDLs) were less than the secondary DWS of  $250,000~\mu\text{g/L}$ . Sulfate concentrations in unfiltered samples are greater than the  $90^{\text{th}}$  percentile Hanford Site background level of  $47,000~\mu\text{g/L}$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, sulfate is not retained as a COPC for further evaluation in the FS.

Metals. Antimony was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and most MDLs were greater than the action level. The action level for antimony is 6 µg/L based on the DWS. Antimony was detected in 5 of 229 unfiltered samples (2.2 percent) and 10 of 224 (4.5 percent) of the filtered groundwater samples. Antimony concentrations in unfiltered samples range between 4.1 and 53 µg/L and filtered groundwater samples range between 0.32 and 75 μg/L. Most unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010 (341 of 453 results). MDLs for results reported by Method 6010 range between 4 and 720 µg/L (283 of 327 MDLs greater than the DWS) and detected concentrations range between 4.1 and 75 µg/L (11 of 14 results greater than DWS). Seven of 14 antimony results reported by Method 6010 were flagged with a "B" qualifier with concentrations ranging between 4.1 and 53 μg/L. Two of 14 antimony results reported by Method 6010 were flagged with a "C" qualifier with concentrations of 47 and 75 µg/L. For samples analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs ranged between 0.3 and 0.6 μg/L and one detected concentration (0.32 µg/L) was reported. All but one detection (in 2008) of antimony are flagged with a "B" or with a "C laboratory qualifier and the presence of antimony does not suggest it is associated with a specific location or a trend. Antimony concentrations reported by trace methods as identified in the 100-D/H SAP (DOE/RL-2009-40) are not above the DWS of 6 μg/L. With the exception of two sample results, one of which is flagged with a "C" qualifier and one unqualified result (60.1 µg/L), all detected antimony concentrations are below the 90th percentile Hanford Site background level of 55 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, antimony is retained as a COPC for further monitoring.

Arsenic was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level and all MDLs were greater than the action level. The action level for arsenic of 0.058  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. However, the analytical method cannot attain the action level; therefore, nondetected concentrations are reported at the EQL of 4  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Arsenic was detected in 52 of 57 (91 percent) of the unfiltered samples and 46 of 51 (90 percent) of the filtered groundwater samples. Arsenic concentrations range between 0.61 and 7.5  $\mu$ g/L in unfiltered groundwater samples and between 0.48 and 7.2  $\mu$ g/L in filtered groundwater samples. Minimum, maximum, and 90<sup>th</sup> percentile concentrations for (filtered) background concentrations of arsenic are 0.5, 8.8, and 7.85  $\mu$ g/L, respectively. All arsenic concentrations in unfiltered and filtered samples are less than the 90<sup>th</sup> percentile Hanford Site background concentration. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, arsenic is not retained as a COPC for further evaluation in the FS.

Beryllium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS, and most MDLs were greater than the DWS of 4  $\mu$ g/L.

Beryllium was detected in 1 of 229 samples (0.44 percent) of the unfiltered samples and in 2 of 224 (0.89 percent) of the filtered groundwater samples. With the exception of 14 MDLs, all beryllium results (detected concentrations and MDLs) were less than the DWS of 4  $\mu$ g/L. Fourteen samples analyzed in 2006 and 2011 were reported with MDLs ranging between 4.1 and 10  $\mu$ g/L; the remaining 436 MDLs were less than or equal to the DWS. In addition, all detected beryllium concentrations were less than the 90<sup>th</sup> percentile Hanford Site background level of 2.3  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC and most MDLs were greater than the AWQC of 0.25 µg/L. Although all monitoring wells within the groundwater area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 5 µg/L. Cadmium was detected in 1 of 229 (0.44 percent) of the unfiltered samples and in 3 of 224 (1.3 percent) of the filtered groundwater samples. Cadmium concentrations in unfiltered and filtered groundwater samples range between 4.3 and 6.1 µg/L. Most unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010 (345 of 453 results) and the MDLs for results reported by Method 6010 range between 0.45 and 30 µg/L (2 of 341 MDLs greater than the DWS and all MDLs greater than the AWQC), and the single unfiltered result is 6 µg/L, and filtered concentrations range between 4.3 and 6.1 µg/L. For samples analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs range between 0.1 and 0.2 µg/L and detected concentrations were not reported. Cadmium was detected in three filtered samples above the AWOC (699-97-43B, 699-99-41, and 699-99-42B) and in one unfiltered sample above the DWS (699-94-41). A single cadmium detection above the DWS was reported in one of 11 sampling rounds conducted at 699-94-41 (6 μg/L); two previous and eight subsequent sample rounds report cadmium as nondetected concentrations below the DWS. A single cadmium detection above the AWQC was reported in one of eight sample rounds conducted at 699-97-43B (6 µg/L); two previous and five subsequent sample rounds report cadmium as nondetected concentrations above the AWOC. A single cadmium detection above the AWQC was reported in one of 15 sampling rounds conducted at 699-99-41 (4.3 µg/L); two previous and 12 subsequent sample rounds report cadmium as nondetected concentrations above the AWQC. A single cadmium detection above the AWQC was reported in one of six sample rounds conducted at 699-99-42B (6.1 µg/L); two previous and three subsequent sample rounds report cadmium as nondetected concentrations above the AWOC. The results of this evaluation indicate that cadmium has historically been detected in groundwater samples at a low frequency (less than 1 percent in unfiltered and 1.3 percent filtered samples), and the presence of cadmium above the AWQC or DWS does not suggest it is associated with a specific location or with a trend. Additionally, cadmium MDLs and detected concentrations reported by Method 6010 are not accurate at concentrations at or near the AWOC. Cadmium concentrations in unfiltered and filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 0.92 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, cadmium is retained as a COPC for further monitoring.

Cobalt was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level, and some MDLs were greater than the action level. The action level for cobalt of 4.8  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Cobalt was detected in 3 of 229 (1.3 percent) of unfiltered samples and 27 of 224 (12 percent) of filtered groundwater samples. Cobalt concentrations in unfiltered samples range between 0.074 and 0.21  $\mu$ g/L and filtered groundwater samples range between 0.06 and 6.2  $\mu$ g/L. Unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010 (345 of 453 results); the MDLs for results reported by Method 6010 range between 1.7

and 70  $\mu$ g/L (43 of 337 MDLs greater than action level). Cobalt was not detected by Method 6010 in unfiltered samples and concentrations ranged between 4 and 6.2  $\mu$ g/L in filtered samples. Some of the results (5 of 8 samples) were flagged with a "B" qualifier, with concentrations ranging between 4 and 6.2  $\mu$ g/L. For samples analyzed using trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), all cobalt results (detected concentrations and MDLs) were less than the action level. Cobalt concentrations above the action level are not associated with a specific location or with a trend. Cobalt results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the action level. However, all cobalt results (detected concentrations and MDLs) reported by trace methods identified in the 100-D/H SAP (DOE/RL-2009-40) are below the action level. Cobalt concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, cobalt is retained as a COPC for further monitoring.

Copper was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWOC, and some MDLs were greater than the AWQC of 9.0 µg/L. Copper was detected in 48 of 229 (21 percent) unfiltered samples and 33 of 224 (15 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640 µg/L. Copper concentrations in unfiltered samples range between 0.1 and 7.6 μg/L and range between 0.23 and 8.8 μg/L in filtered groundwater samples. All copper results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Filtered samples collected for purposes other than the RI were analyzed by Method 6010 (173 of 224 results). The MDLs for results reported by Method 6010 range between 2.8 and 70 µg/L (1 of 329 MDLs greater than AWQC), and filtered concentrations ranged between 4 and 7 µg/L. For samples analyzed using the trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs range between 0.1 and 0.2 μg/L and filtered concentrations range between 0.23 and 8.8 µg/L. Two MDLs associated with historical concentrations (reported by Method 6010) are not accurate at concentrations at or near the AWOC. All copper results (detected concentrations and MDLs) reported by trace methods identified in the 100-D/H SAP (DOE/RL-2009-40) are below the AWOC. Copper concentrations in filtered samples are above the 90th percentile Hanford Site background level of 0.81 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, copper is retained as a COPC for further monitoring.

Iron was detected in 147 of 225 (65 percent) of unfiltered and 60 of 224 (27 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater area were compared to the AWQC of 1,000 μg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200 μg/L. All samples were analyzed by Method 6010 as identified in the 100-D/H SAP (DOE/RL-2009-40). Iron concentrations in unfiltered samples range between 12 and 2,840 μg/L and range between 11 and 2,050 μg/L in filtered samples. All unfiltered iron results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standard's" [WAC 173-340-720]) groundwater cleanup level. Except for iron concentrations reported at well 699-90-45, all filtered iron results (detected concentrations and MDLs) are less than the AWQC. All three filtered samples analyzed for iron reported iron concentrations above the AWQC at well 699-90-45, with concentrations ranging between 1,780 and 2,050 μg/L. The results of this evaluation indicate that iron concentrations have historically been detected in groundwater. Iron concentrations above the AWQC of 1,000 μg/L at 699-90-45 are a result of the corrosion of the carbon steel well casing that was installed in 1961. Except for iron reported at 699-90-45, iron concentrations in filtered water samples are less than

the background level of 570  $\mu$ g/L. Iron concentrations measured in well 699-90-45 are not greater than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Additionally, this well is located inland and is not expected to impact the Columbia River. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, iron is not retained as a COPC for further evaluation in the FS.

Lead was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standard (WAC 173-201A), and some MDLs were greater than the standard of  $2.1 \,\mu g/L$ . Lead was detected in 7 of 57 (12 percent) of unfiltered and 2 of 51 (3.9 percent) of filtered groundwater samples. Although all monitoring wells within the Horn area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 15  $\mu g/L$ . All lead results (detected concentrations and MDLs) are less than the DWS and the state water quality standard. Lead concentrations in unfiltered and filtered samples are less than the  $90^{th}$  percentile Hanford Site background level of  $0.92 \,\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, lead is not retained as a COPC for further evaluation in the FS.

Manganese was detected in 58 of 229 (25 percent) of unfiltered and 46 of 224 samples (21 percent) of filtered groundwater. The action level for manganese of 384  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All manganese results (detected concentrations and MDLs) were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 384  $\mu$ g/L. Manganese concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 39  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, manganese is not retained as a COPC for further evaluation in the FS.

Mercury was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC, and some MDLs were greater than the AWQC of  $0.012~\mu g/L$ . The analytical method for mercury cannot attain the AWQC; therefore, nondetected concentrations are reported at the EQL of  $0.5~\mu g/L$  identified in the 100-D/H SAP (DOE/RL-2009-40). Mercury was not detected in any unfiltered (52 samples) or filtered (52 samples) groundwater samples. All MDLs are less than the EQL of  $0.5~\mu g/L$  identified in the 100-D/H SAP (DOE/RL-2009-40). MDLs for mercury in filtered samples are above the  $90^{th}$  percentile Hanford Site background level of  $0.003~\mu g/L$ . Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, mercury is not retained as a COPC for further evaluation in the FS.

Nickel was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC of 52  $\mu$ g/L. Nickel was detected in 17 of 229 (7.4 percent) of unfiltered and 13 of 224 (5.8 percent) of filtered groundwater samples. Although all monitoring wells within the Horn area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. Nickel concentrations in unfiltered samples range between 0.20 and 12  $\mu$ g/L and filtered groundwater samples range between 4 and 19  $\mu$ g/L. All nickel results (detected concentrations and MDLs) are less than the DWS. All detected nickel concentrations in filtered samples are less than the AWQC however, six MDLs for filtered samples were greater than the AWQC (MDLs ranged between 66.5 and 133  $\mu$ g/L). All samples were analyzed by Method 6010 as identified in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). All detected concentrations and all but six MDLs were less than the AWQC. Nickel concentrations in filtered samples are above the 90th percentile Hanford Site background level of 1.6  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, nickel is not retained as a COPC for further evaluation in the FS.

Selenium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the AWQC of 5  $\mu$ g/L, and some MDLs were greater than the AWQC. Selenium was detected in 50 of 57 (88 percent) of unfiltered and 49 of 51 (96 percent) of filtered groundwater samples. Although all monitoring wells within the Horn area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 50  $\mu$ g/L. Selenium concentrations in unfiltered samples ranged between 0.91 and 7.1  $\mu$ g/L and filtered samples ranged between 0.78 and 7.3  $\mu$ g/L. All selenium results (detected concentrations and MDLs) are less than the DWS. Selenium concentrations in filtered samples above the AWQC were reported at 699-95-51. Selenium was detected once at 699-95-51 in a filtered (7.3  $\mu$ g/L) sample; however, two subsequent sample rounds are less than the AWQC. All selenium concentrations are less than the 90<sup>th</sup> percentile Hanford Site background level of 11  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, selenium is not retained as a COPC for further evaluation in the FS.

Silver was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standard (WAC 173-201A), and some MDLs were greater than the standard of 2.6 µg/L. The analytical method cannot attain the state water quality standard of 2.6 µg/L; therefore, nondetected concentrations are reported at the EQL of 10 µg/L identified in the 100-D/H SAP (DOE/RL-2009-40). Silver was detected in 5 of 229 (2.2 percent) of unfiltered and 5 of 224 (2.2 percent) of filtered groundwater samples. Although all monitoring wells within the Horn area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80 µg/L. Silver concentrations in unfiltered samples ranged between 0.28 and 12 μg/L and filtered groundwater samples ranged between 5.6 and 13 µg/L. All detected concentrations and all but two MDLs were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80 μg/L. Unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010 (345 of 453 results). The MDLs for samples analyzed by Method 6010 ranged between 2.2 and 110 µg/L and detected concentrations from filtered samples ranged between 5.6 and 13 µg/L. All five detected silver results reported by Method 6010 were flagged with a "B" qualifier and one was flagged with both a "B" and a "C" qualifier. The single silver concentration flagged with a "BC" was 8.2 µg/L. For samples analyzed by trace methods identified in the 100-D/H SAP (DOE/RL-2009-40), the MDLs range between 0.1 and 0.2 µg/L and silver was not detected in filtered samples. All historical detections of silver for filtered samples are flagged with a combination of "B" and "C" qualifiers. Silver concentrations are not associated with a specific location or a trend. Silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the state water quality standard. All silver results (detected concentrations and MDLs) reported by trace methods identified in the 100-D/H SAP (DOE/RL-2009-40) are less than the state water quality standard of 2.6 µg/L and are also below the 90<sup>th</sup> percentile Hanford Site background level of 5.3 μg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, silver is retained as a COPC for further monitoring.

Thallium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS goal, and some MDLs were greater than the DWS goal of 0.5  $\mu$ g/L. The analytical method cannot attain the DWS goal of 0.5  $\mu$ g/L; therefore, nondetected concentrations are reported at the EQL of 2  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Thallium was not detected in any of the unfiltered (57 samples) or filtered samples (51 samples). All MDLs are less than the EQL of 2  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). Based on

the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, thallium is not retained as a COPC for further evaluation in the FS.

Uranium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the DWS of 30  $\mu$ g/L. Uranium was detected in all 55 unfiltered samples and all 16 filtered groundwater samples. All uranium results (detected concentrations and MDLs) are less than the DWS of 30  $\mu$ g/L. Uranium concentrations in unfiltered and filtered samples are less than the 90<sup>th</sup> percentile Hanford Site background level of 9.9  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, uranium is not retained as a COPC for further evaluation in the FS.

Vanadium was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the action level of 80  $\mu$ g/L. The action level for vanadium of 80  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Vanadium was detected in 93 of 229 (41 percent) of unfiltered samples and 85 of 224 (38 percent) of filtered groundwater samples. Vanadium concentrations in filtered and unfiltered samples range between 4.2 and 38  $\mu$ g/L, which are below the action level. All detected concentrations and all but two MDLs were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Two samples collected from well 699-97-43 during 2006 and analyzed by Method 6010 were reported with MDLs of 140  $\mu$ g/L. Vanadium concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 12  $\mu$ g/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, vanadium is not identified as a COPC for further evaluation in the FS.

Zinc was identified as a historical COPC in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1) because it was detected above the state water quality standard (WAC 173-201A), and some MDLs were greater than the standard of 91 µg/L. Zinc was detected in 32 of 229 (14 percent) unfiltered and 31 of 224 (9.4 percent) filtered groundwater samples. All samples were analyzed by Method 6010 as identified in the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). Although all monitoring wells within the Horn area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 µg/L. All zinc results (detected concentrations and MDLs) were less than the 2007 MTCA groundwater cleanup level. Zinc concentrations in filtered samples range between 4 and 364 µg/L. Zinc concentrations in filtered samples above the state water quality standard were reported at four wells (699-87-55, 699-97-43, 699-99-41, and 699-99-42B). Zinc concentrations above the state water quality standard were reported in one of seven sample rounds at 699-87-55 (364 µg/L); however, four previous and two subsequent rounds were less than the standard. Zinc concentrations in filtered samples above the state water quality standard were reported in one of three sample rounds at 699-97-43 (93 µg/L); however, one previous and one subsequent sample round were less than the standard. Zinc concentrations above the state water quality standard were reported in one of six sample rounds at 699-99-42B (306 µg/L); however, five previous sample rounds were reported as nondetected concentrations less than the action level. Zinc concentrations above the action level in these four wells are not associated with a trend. Zinc concentrations are also greater than the 90<sup>th</sup> percentile Hanford Site background level of 22 µg/L. Based on the results of this evaluation and the results of the groundwater risk assessment presented in Section 6.3, zinc is not retained as a COPC for further evaluation in the FS.

**Summary of the Horn Groundwater Area Groundwater Evaluation.** Table 4-11 summarizes the outcome of the analysis. Contaminants that warrant further evaluation in the FS are chromium (total) and Cr(VI). Groundwater contaminants that do not warrant further evaluation in the FS, but have infrequent detections

above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency.

Table 4-11. Summary of Horn Groundwater Area Contaminant Evaluation

Category	Constituent
Retained as	a COPC
Contaminant of potential concern* (contaminants that warrant further evaluation in FS)	Chromium, Cr(VI)
Retained for I	Monitoring
Detected at levels above action level and background	Antimony, cadmium, carbon tetrachloride, cobalt, copper, silver
Not Retained	as a COPC
Detected in groundwater but below action level, EQL, or background concentrations	Arsenic, beryllium, chloroform, fluoride, gross alpha, gross beta, iron, lead, manganese, nickel, nitrate, nitrite, selenium, sulfate, strontium-90, technetium-99, trichloroethene, tritium, uranium, vanadium, zinc
Not detected in groundwater	1,1-Dichloroethene, benzene, cesium-137, cobalt-60, europium-152. europium-154, europium-155, mercury, thallium, vinyl chloride

<sup>\*</sup> Based on evaluation of data collected January 2006 through December 2012.

COPC = contaminant of potential concern

EQL = estimated quantitation limit

FS = feasibility study

**Additional Analytes Requested by Agencies.** As described earlier, additional analytes and sample locations were added through Step 4 of the COPC identification process described in Section 4.4 of the 100-D/H Work Plan (DOE/RL-2008-46-ADD1). Table 4-8 lists the additional groundwater analytes and locations for analysis. In general, the following analytical methods were added:

- Pesticides by Method 8081 at three well locations
- PCBs by Method 1668A at six well locations
- PCBs by Method 8082 at 16 well locations
- PAHs by Method 8310 at 16 well locations
- SVOCs by Method 8270 at 16 well locations
- Radionuclides at all well locations within the monitoring well network
- Cyanide by Method 9012 at one well location

The following describes the analytes from each of the methods including pesticides, dioxin-like PCB congeners, PCB aroclors, PAHs, SVOCs, and radionuclides (discussed in previous section). The following subsection discusses the results of the additional analytes and well locations by analytical method. Summary statistics for each well representing the additional analytes are presented in Tables N-4 through N-19.

**Pesticides by Method 8081.** Pesticides were analyzed at three wells including 199-D5-15, 199-D8-71, and 199-H4-48. Pesticides were not detected in any of the samples analyzed.

Dioxin-like PCB Congeners by Method 1668A. Dioxin-like PCB congeners were analyzed at the following 6 wells: 199-D5-15, 199-D8-55, 199-D8-71, 199-H4-10, 199-H4-13, and 199-H4-48. There are twelve dioxin-like PCB congeners, which have associated toxicity information allowing the calculation of an action level. The following discusses only these twelve PCB congeners:

- Two PCB congeners were detected at 199-D5-15, both at concentrations less than their action level.
- One PCB congener was detected at 199-H4-10 and 199-H4-48 at concentrations less than its action level.
- Two PCB congeners were detected at 199-D8-55 at concentrations less than their respective action level.
- Five PCB congeners were detected at 199-D8-71, all at concentrations less than their action level.
- Seven PCB congeners were detected at 199-H4-13 with six of seven PCB congeners at concentrations less than their action level.
- One PCB congener (2,3',4,4',5-Pentachlorobiphenyl) was detected in 199-H4-13 at a concentration greater than the action level during the low river stage; however, two subsequent rounds reported the congener as nondetected or at a concentration less than the action level.

**PCB Aroclors by Method 8082.** PCB aroclors were analyzed at the following 16 wells: 199-D4-84, 199-D5-13, 199-D5-15, 199-D5-17, 199-D5-99, 199-D8-55, 199-D8-71, 199-D8-88, 199-H3-2A, 199-H4-10, 199-H4-11, 199-H4-13, 199-H4-16, 199-H4-3, 199-H4-45, and 199-H4-48. PCB aroclors were not detected in any of the samples analyzed.

**Polynuclear Aromatic Hydrocarbons by Method 8310.** PAHs were analyzed at the following 16 wells: 199-D4-84, 199-D5-13, 199-D5-15, 199-D5-17, 199-D5-99, 199-D8-5, 199-D8-71, 199-D8-88, 199-H3-2A, 199-H4-10, 199-H4-11, 199-H4-13, 199-H4-16, 199-H4-3, 199-H4-45, and 199-H4-48. PAHs were not detected in any of the samples analyzed.

**Semivolatile Organic Compounds by Method 8270.** SVOCs were analyzed at the following 16 wells: 199-D4-84, 199-D5-13, 199-D5-15, 199-D5-17, 199-D5-99, 199-D8-55, 199-D8-71, 199-D8-88, 199-H3-2A, 199-H4-10, 199-H4-11, 199-H4-13, 199-H4-16, 199-H4-3, 199-H4-45, and 199-H4-48. Except for one well, SVOCs were either not detected or detected at concentrations less than the action level.

Bis(2-ethylhexyl)phthalate was detected in one of three samples collected from 199-D8-88 at a concentration (2.1  $\mu$ g/L) above the action level of 1.2  $\mu$ g/L. Bis(2-ethylhexyl)phthalate is a common laboratory contaminant that is introduced into the sample after it is collected in the field.

**Cyanide by Method 9012.** Cyanide was analyzed at well 199-H4-3. Cyanide was not detected in any of the three sampling rounds performed at this well.

Conclusions for Additional Analytes. The following summarizes the conclusions that can be made from the evaluation presented above and identifies uncertainties associated with the results of the evaluation. Additional analytical methods were added for up to 16 well locations and include the following types of analyte classes: pesticides, dioxin-like PCB congeners, PCB aroclors, PAHs, SVOCs, cyanide, and radionuclides (summarized previously).

- Pesticides, PCB aroclors, and PAHs were not detected in any of the samples analyzed.
- Dioxin-like PCB congeners were detected at least once in five wells but detected concentrations were less than the action level. A dioxin-like PCB congener was detected once at concentrations above the action level at one well but is not associated with a trend.
- Except for one well, SVOCs were either not detected or detected at concentrations less than the action level. Bis(2-ethylhexyl)phthalate was detected in one of three samples collected from 199-D8-88 at a concentration (2.1 μg/L) above the action level of 1.2 μg/L. Bis(2-ethylhexyl)phthalate is a common laboratory contaminant that is introduced into the sample after it is collected in the field.
- Cyanide was not detected in any of the samples analyzed (three sampling rounds at one well).

## 4.4.1.3 Groundwater Evaluation for the Confined Aquifer

The nature and extent of contamination in groundwater in the confined aquifer was based on the last 7 years of data (samples collected between January 1, 2006 and December 31, 2012). The nature and extent evaluation described in this section uses data for wells screened in the first water bearing unit of the RUM. A total of 12 wells were included in the evaluation and are listed in Table 4-12. Figure 4-67 provides the locations of the wells considered in the nature and extent evaluation. Groundwater data for 100-D/H were compiled and statistically analyzed and the results are presented in Appendix N (Tables N-20 through Table N-22). These tables present the summary statistics for each analyte where data were available from the completed well and met the 7-year period criteria. The tables also list the background concentrations in Hanford Site groundwater (*Hanford Site Background: Part 3, Groundwater Background* [DOE/RL-96-61]) where available, and the corresponding action level.

Table 4-12. Monitoring Wells Constructed in the Confined Aquifer (First Water Bearing Unit of the Ringold Formation Upper Mud)

100-D Area	100-H Area	Horn Area
199-D5-134	199-H2-1	699-97-43C
199-D5-141	199-H3-2C	699-97-45B
199-D8-54B	199-H3-9	699-97-48C
	199-H3-10	
	199-H4-12C	
	199-H4-15CS	

The evaluation of the data for the confined aquifer is similar to that performed for the unconfined aquifer. The results summary is provided in the following subsections for the 100-D groundwater area, the 100-H groundwater area, and the Horn groundwater area.

**Confined Aquifer Analytes—100-D Area.** The following subsections describe the analytical data that were available from completed wells and met the 7-year time frame criteria at 100-D, and includes radionuclides, anions, and metals. These analytes include all data collected during the specified period.

**Radionuclides.** Gross alpha and gross beta were analyzed in all of the confined aquifer wells. Gross alpha was detected in 22 percent of the groundwater samples and gross beta was detected in 100 percent of the samples. Gross alpha was detected at concentrations ranging between 2.2 and 3.3 pCi/L, which are less than the DWS of 15 pCi/L. Gross beta was detected at concentrations ranging between 5.2 and 13 pCi/L. While the concentrations of strontium-90 were not analyzed, gross beta had a maximum value of

13 pCi/L; therefore, the presence of strontium-90 is not expected. Based on the results of this evaluation, gross alpha and gross beta are not retained as COPCs for further evaluation in the FS.

Tritium was analyzed because it was detected in the unconfined aquifer above the DWS of 20,000 pCi/L. Tritium was detected in one of the nine groundwater samples (11 percent) collected from the confined aquifer wells. All results (detected concentrations and MDLs) are less than the DWS of 20,000 pCi/L. Based on the results of this evaluation, tritium is not retained for further evaluation in the FS.

**Anions.** Fluoride was detected in eight of nine (89 percent) of groundwater samples with concentrations ranging between 92  $\mu$ g/L and 408  $\mu$ g/L. The action level of 960  $\mu$ g/L for fluoride is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All fluoride results (detected concentrations and MDLs) are less than the action level and the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Based on the results of this evaluation, fluoride is not retained for further evaluation in the FS.

Nitrate was detected in six of nine (67 percent) of groundwater samples with concentrations ranging between 837  $\mu$ g/L and 2,528  $\mu$ g/L. All nitrate results (detected concentrations and MDLs) are less than the DWS. Based on the results of this evaluation, nitrate is not retained for further evaluation in the FS for the confined aquifer.

Nitrite was detected in three of nine (33 percent) of groundwater samples with concentrations ranging between 175  $\mu$ g/L and 298  $\mu$ g/L. All nitrite results (detected concentrations and MDLs) are less than the DWS. Nitrite concentrations are greater than the 90th percentile Hanford Site background level of 94  $\mu$ g/L. Based on the results of this evaluation, nitrite is not retained for further evaluation in the FS.

Sulfate was detected in all nine (100 percent) groundwater samples with concentrations ranging between 11,500  $\mu$ g/L and 66,000  $\mu$ g/L. All but two sulfate results are greater than the 90th percentile Hanford Site background level of 47,014  $\mu$ g/L; all are less than the secondary DWS. Based on the results of this evaluation, sulfate is not retained for further evaluation in the FS.

**Metals.** Antimony was not detected in any of nine unfiltered or filtered groundwater samples. Most unfiltered and filtered samples collected for purposes other than the RI were analyzed by Method 6010. The action level for antimony is 6  $\mu$ g/L based on the DWS. MDLs for samples analyzed by Method 6010 ranged between 4 and 72  $\mu$ g/L (16 of 18 MDLs were greater than the DWS). All but four MDLs are less than the 90<sup>th</sup> percentile Hanford Site background level of 55  $\mu$ g/L. Antimony MDLs reported by Method 6010 are not accurate at concentrations at or near the DWS. Based on these uncertainties, antimony is retained as a COPC for further monitoring.

Arsenic was detected in the single unfiltered and filtered groundwater sample. Both samples report arsenic concentrations of 4.2  $\mu$ g/L. Both arsenic concentrations in unfiltered and filtered samples are less than the 90<sup>th</sup> percentile Hanford Site background concentration. Based on the results of this evaluation, arsenic is not retained as a COPC for further evaluation in the FS.

Beryllium was not detected in any of the nine unfiltered or filtered samples. All MDLs were less than or equal to the DWS. Beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was not detected in any of the nine unfiltered or filtered samples. All samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 0.91 and 4  $\mu$ g/L (all greater than the AWQC and less than the DWS). Cadmium MDLs reported by Method 6010 are not accurate at concentrations at or near the AWQC. Based on these uncertainties, cadmium is retained as a COPC for further monitoring.

Chromium was detected in four of nine (44 percent) of unfiltered samples and one of nine (11 percent) of filtered groundwater samples. Detected chromium concentrations range between 3.4 and 11  $\mu$ g/L in unfiltered samples and measured 5.8  $\mu$ g/L in the filtered sample. Total chromium concentrations are less than the AWQC and DWS. All MDLs were less than the AWQC and DWS. Chromium is not retained as a COPC for further evaluation in the FS.

Cobalt was not detected in any of the nine unfiltered or filtered samples. The action level for cobalt of  $4.8 \,\mu\text{g/L}$  is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All samples were analyzed by Method 6010. With the exception of two MDLs, the remaining 16 MDLs were less than the action level. Based on the results of this evaluation, cobalt is not retained as a COPC for further evaluation in the FS.

Copper was detected in one of nine unfiltered samples (11 percent) and was not detected in any of the nine filtered groundwater samples. The detected concentration of copper measured 4  $\mu$ g/L, which is above the background value of 0.81  $\mu$ g/L, but less than the AWQC. All MDLs were less than the AWQC. Based on the results of this evaluation, copper is not retained as a COPC for further evaluation in the FS.

Cr(VI) was detected in five of 11 (45 percent) of unfiltered samples and four of six (67 percent) of the filtered groundwater samples. Cr(VI) concentrations detected in unfiltered samples range between 2.7 and 15  $\mu$ g/L and range between 2 and 9  $\mu$ g/L in the filtered samples. The Cr(VI) concentration in one unfiltered sample measured above the state surface water quality standard (WAC 173-201A) of 10  $\mu$ g/L. All MDLs were less than or equal to the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L and the state surface water quality standard. Based on the uncertainty associated with one sample result above the standard, Cr(VI) is retained as a COPC for further evaluation in the FS.

Iron was detected in eight of nine (89 percent) of unfiltered and seven of nine (78 percent) of filtered groundwater samples. Iron concentrations in unfiltered samples range between 48 and 1,190  $\mu$ g/L and range between 25 and 1,140  $\mu$ g/L in filtered samples. Although all monitoring wells within the groundwater area were compared to the AWQC of 1,000  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200  $\mu$ g/L. With the exception of iron measured in the filtered (1,140  $\mu$ g/L) and unfiltered sample (1,190  $\mu$ g/L) from well 199-D-134, all iron concentrations are less than the AWQC and the 90<sup>th</sup> percentile Hanford Site background concentration of 570  $\mu$ g/L. Iron is not retained as a COPC for further evaluation in the FS.

Manganese was detected in six of nine (67 percent) of unfiltered and five of nine samples (56 percent) of filtered groundwater samples. Manganese concentrations in unfiltered samples range between 4 and 853  $\mu g/L$  and between 4.9 and 865  $\mu g/L$  in filtered groundwater samples. The action level for manganese of 384  $\mu g/L$  is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. With the exception of manganese measured in the filtered (865  $\mu g/L$ ) and unfiltered sample (853  $\mu g/L$ ) from well 199-D5-134, all manganese concentrations are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level and the 90<sup>th</sup> percentile Hanford Site background level of 39  $\mu g/L$ . Manganese is not retained as a COPC for further evaluation in the FS.

Nickel was not detected in any of the nine unfiltered and was detected in one of nine filtered samples (11 percent). With the exception of one MDL, all nickel results (detected concentrations and MDLs) are less than the AWQC. The single detected nickel concentration and MDLs are above the 90<sup>th</sup> percentile

Hanford Site background level of 1.6  $\mu$ g/L. Nickel is not retained as a COPC for further evaluation in the FS.

Silver was not detected in any of the nine unfiltered or filtered samples. All samples were analyzed by Method 6010. Although all monitoring wells within the area were compared to the state water quality standard of 2.6  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. MDLs for samples analyzed by Method 6010 ranged between 4 and 11  $\mu$ g/L (all greater than the AWQC and all less than the groundwater cleanup level). Silver MDLs reported by Method 6010 are not accurate at concentrations at or near the AWQC. Based on these uncertainties, silver is retained as a COPC for further monitoring.

Uranium was detected in the single unfiltered sample (100 percent). Filtered groundwater samples were not analyzed. The uranium result (3.2  $\mu$ g/L) is less than the background concentration and DWS. Uranium is not retained as a COPC for further evaluation in the FS.

Vanadium was detected in eight of nine (89 percent) unfiltered and all nine (100 percent) filtered groundwater samples. The concentrations in the unfiltered and filtered samples range between 5.5 and 46  $\mu$ g/L, respectively. All but four vanadium results (detected concentrations and MDLs) are greater than the background concentration and all are less than the action level of 80  $\mu$ g/L. Vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was detected in six of nine (67 percent) unfiltered and five of nine (56 percent) filtered groundwater samples. Zinc concentrations in unfiltered samples range between 6.3 and 756 μg/L and range between 7.1 and 439 in filtered groundwater samples. Although all monitoring wells within the area were compared to the state water qua[ity standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 μg/L. All zinc results (detected concentrations and MDLs) were less than the 2007 MTCA groundwater cleanup level. Zinc was detected above the AWQC in all three of the filtered samples from 199-D5-141 (253 to 439 μg/L). Zinc is retained as a COPC for further monitoring.

Data are also available for barium, calcium, magnesium, potassium sodium, and strontium, which are not retained for further analysis. Calcium, magnesium, potassium, and sodium are essential nutrients, and the barium and strontium concentrations are below their 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720) groundwater cleanup levels.

**Confined Aquifer Analytes—100-H Area.** The following subsections describe the analytical data that were available from completed wells and met the 7-year period criteria and include radionuclides, VOCs, anions, and metals. These analytes include all data collected during the specified period.

**Radionuclides.** Gross alpha and gross beta were analyzed in three of the six confined aquifer wells. Gross alpha was detected in 8.3 percent of the groundwater samples and gross beta was detected in 92 percent of the samples. Gross alpha was detected at a concentration of 2.5 pCi/L, which is less than the DWS of 15 pCi/L. Gross beta was detected at concentrations ranging between 3.8 and 14 pCi/L. Gross beta concentrations are generally consistent with the presence of tritium or strontium-90. Based on the results of this evaluation, gross alpha and gross beta are not retained as COPCs for further evaluated in the FS.

Strontium-90 was detected in two of 16 (12 percent) of the groundwater samples with concentrations ranging between 1.7 and 2.2 pCi/L. Strontium-90 concentration was measured in Well 199-H3-9 and Well 199-H3-10. All results (detected concentrations and MDLs) are less than the DWS of 8 pCi/L. Strontium-90 is not retained as a COPC for further evaluation in the FS.

Technetium-99 was detected in 2 of 23 (8.7 percent) of the groundwater samples with concentrations ranging between 7.9 and 12 pCi/L. All results (detected concentrations and MDLs) are less than the DWS of 900 pCi/L. The highest technetium-99 concentration was measured in Well 199-H4-12C. Technetium-99 is not retained as a COPC for further evaluation in the FS.

Tritium was detected in 4 of 25 (16 percent) of the groundwater samples with concentrations ranging between 270 and 1,800 pCi/L. All results (detected concentrations and MDLs) are less than the DWS of 20,000 pCi/L. The highest tritium concentration was measured in well 199-H3-2C. Tritium is not retained as a COPC for further evaluation in the FS.

Cesium-137, cobalt-60, europium-152, europium-154, and europium-155 were not detected in any of the samples collected from the confined aquifer in the 100-H Area, and all MDLs were less than their DWS. Based on the results of this evaluation, cesium-137, cobalt-60, europium-152, europium-154, and europium-155 are not retained as COPCs for further evaluation in the FS.

Data are also available for other radionuclides that are not retained for further analysis. Beryllium-7, cesium-134, and ruthenium-106 have half-lives less than three years. Potassium-40 levels are attributable to background radiation levels, and antimony-125 has no defined action level.

**Volatile Organic Compounds.** 1,1-Dichloroethene, benzene, carbon tetrachloride, trichloroethene, and vinyl chloride were not detected in any of the samples collected from the confined aquifer in the 100-H Area, and the MDLs were less than or equal to their action level or EQL (as applicable). Based on the results of this evaluation, 1,1-dichloroethene, benzene, carbon tetrachloride, chloroform, trichloroethene, and vinyl chloride are not retained as COPCs for further evaluation in the FS.

Chloroform was detected in all six (100 percent) of the groundwater samples with a concentrations ranging between 2.6 and 4.2  $\mu$ g/L. The action level for chloroform of 1.4  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The analytical method cannot attain the action level for chloroform; therefore, nondetected concentrations are reported at the EQL of 5  $\mu$ g/L identified in the 100-D/H SAP (DOE/RL-2009-40). All chloroform results (detected concentrations and MDLs) are less than the EQL. Chloroform is not retained as a COPC for further evaluation in the FS.

Data are also available for 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,2-dichloroethane, 1,4-dichlorobenzene, 1,4-dioxane, 1-butanol, 2-butanone, 2-hexanone, 4-methyl-2-pentanone, acetone, bromoform, bromomethane, carbon disulfide, chlorobenzene, chloroethane, chloromethane, cis-1,2-dichloroethylene, cis-1,3-dichloropropene, dibromochloromethane, ethyl cyanide, ethylbenzene, methylene chloride, styrene, tetrahydrofuran, toluene, trans-1,2-dichloroethylene, trans-1,3-dichloropropene, and xylenes (total), but none of these organics were detected or retained as COPCs for further evaluation in the FS.

**Anions.** Fluoride was detected in 20 of 26 (77 percent) of groundwater samples with concentrations ranging between 26  $\mu$ g/L and 230  $\mu$ g/L. All fluoride results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 960  $\mu$ g/L and the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Fluoride is not retained as a COPC for further evaluation in the FS.

Nitrate was detected in all 26 (100 percent) of the groundwater samples with concentrations ranging between 770  $\mu$ g/L and 21,500  $\mu$ g/L. All nitrate results of detected concentrations are less than the DWS and the 90th percentile Hanford Site background level of 26,871  $\mu$ g/L. Nitrate is not retained as a COPC in the confined aquifer for further evaluation in the FS.

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Nitrite was detected in 8 of 26 (31 percent) of groundwater samples at concentrations ranging between 141 and 348  $\mu$ g/L. All nitrite results (detected concentrations and MDLs) are less than the DWS, but concentrations are greater than the 90th percentile Hanford Site background level of 94  $\mu$ g/L. Nitrite is not retained as a COPC for further evaluation in the FS.

Sulfate was detected in all 26 (100 percent) of the groundwater samples with concentrations ranging between 20,200  $\mu$ g/L and 74,500  $\mu$ g/L. All sulfate results are less than the secondary DWS, but concentrations are greater than the 90th percentile Hanford Site background level. Sulfate is not retained as a COPC for further evaluation in the FS.

Data are also available for other anions that are not retained for further analysis. There are no action levels for bromide or phosphate, and chloride and cyanide concentrations are all below the Clean Water Act - Freshwater Criterion Continuous Concentration (CCC).

**Metals.** Antimony was detected in 2 of 30 unfiltered samples (6.7 percent) and none of the 21 filtered groundwater samples. Antimony concentrations in unfiltered samples range between 0.48 and 4.3 μg/L in the unfiltered samples. MDLs range between 0.6 and 72 μg/L. The action level for antimony is 6 μg/L based on the DWS. All detected antimony concentrations are less than the DWS. All MDLs reported by Method 200.8 are less than the DWS. A total of 42 of 51 samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 4 and 72 μg/L (40 of 42 MDLs were greater than the DWS). Antimony MDLs reported by Method 6010 are not accurate at concentrations at or near the DWS. All detected antimony concentrations and 43 of 49 MDLs are below the 90<sup>th</sup> percentile Hanford Site background level of 55 μg/L. Based on these uncertainties, antimony is retained as a COPC for further monitoring.

Arsenic was detected in all five (100 percent) of the unfiltered groundwater samples. Arsenic concentrations range between 2.3 and 3.4  $\mu$ g/L in the unfiltered samples. The arsenic concentrations are less than the 90<sup>th</sup> percentile Hanford Site background concentration. Based on the results of this evaluation, arsenic is not retained as a COPC for further evaluation in the FS.

Beryllium was not detected in any of the 26 unfiltered or 21 filtered groundwater samples. All beryllium MDLs were less than or equal to the DWS of 4  $\mu$ g/L. Beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was not detected in any of the 30 unfiltered or 21 filtered samples. Although all monitoring wells within the groundwater area were compared to the AWQC of  $0.25~\mu g/L$ , these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of  $5~\mu g/L$ . All MDLs (9 samples) reported by Method 200.8 were less than the AWQC. A total of 42 of 51 samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 0.91 and  $4~\mu g/L$ ; all are greater than the AWQC and all are less than the DWS. Cadmium MDLs reported by Method 6010 are not accurate at concentrations at or near the AWQC. Based on these uncertainties, cadmium is retained as a COPC for further monitoring.

Total chromium was detected in 26 of 30 (87 percent) of unfiltered samples and 17 of 21 (81 percent) of filtered groundwater samples. Chromium concentrations in unfiltered samples range between 3.6 and 164  $\mu$ g/L and filtered samples range between 7 and 158  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 65  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. Chromium concentrations in filtered samples above the AWQC of 65  $\mu$ g/L were reported at four wells (199-H3-9, 199-H4-12C, 199-H4-15CS, and 199-H3-2C). Chromium concentrations in unfiltered samples above the DWS of 100  $\mu$ g/L were reported at three wells (199-H3-9, 199-H4-12C, and 199-H4-15CS).

Chromium concentrations above the AWQC (and DWS) were reported in all three sampling rounds at 199-H3-9. Chromium concentrations in filtered samples were above the AWQC in all seven sampling rounds and unfiltered samples were above the DWS in six of nine rounds at 199-H4-12C. Chromium concentrations in filtered samples were above the AWQC in all three sampling rounds and unfiltered samples were above the DWS in one of three rounds at 199-H4-15CS. Chromium concentrations in filtered samples were above the AWQC in one of five sampling rounds and unfiltered samples were less the DWS in all three rounds at 199-H3-2C. Chromium is retained as a COPC for further evaluation in the FS.

Cobalt was detected in 2 of 30 unfiltered samples (8.3 percent) and none of the 21 filtered groundwater samples. Cobalt was measured at concentrations of 0.073 and 0.11  $\mu$ g/L, which is below the action level. The action level for cobalt of 4.8  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All MDLs (9 samples) reported by Method 200.8 were less than the action level. A total of 42 of 51 samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 4 and 7  $\mu$ g/L (6 of 42 MDLs were greater than the action level). Some of the cobalt MDLs reported by Method 6010 are not accurate at concentrations at or near the action level. Based on the results of this evaluation, cobalt is not retained as a COPC for further monitoring.

Copper was detected in 11 of 30 unfiltered samples (37 percent) and 3 of 21 filtered groundwater samples (14 percent). Although all monitoring wells within the groundwater area were compared to the AWQC of 9  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640  $\mu$ g/L. Copper concentrations in unfiltered samples range between 0.2 and 21  $\mu$ g/L and filtered groundwater samples range between 8 and 22  $\mu$ g/L. All copper results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. No filtered samples were analyzed by Method 200.8. All MDLs for filtered samples were less than the AWQC. Copper was reported above the AWQC in two wells (199-H3-2C and 199-H4-12C). Copper concentrations in filtered samples were above the AWQC in one of three sampling rounds at 199-H3-2C and in one of seven rounds at 199-H4-12C. Based on the results of this evaluation, copper is not retained as a COPC for further evaluation in the FS.

Cr(VI) was detected in 109 of 117 (93 percent) of unfiltered samples and all 15 of filtered groundwater samples. Cr(VI) concentrations in unfiltered samples range between 2.1 and 179 μg/L and filtered samples range between 62 and 140 μg/L. Although all monitoring wells within the groundwater area were compared to the state surface water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48 μg/L. Cr(VI) concentrations in filtered samples above the state surface water quality standard of 10 μg/L were reported at 199-H3-2C, 199-H4-12C, and 199-H4-15CS. Cr(VI) concentrations in unfiltered samples above the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level were reported at 199-H3-2C, 199-H3-9, 199-H4-12C, and 199-H4-15CS. Cr(VI) is retained as a COPC for further evaluation in the FS.

Iron was detected in 11 of 23 (48 percent) of unfiltered and 5 of 21 (24 percent) of filtered groundwater samples. Iron concentrations in unfiltered samples range between 12 and  $56 \mu g/L$  and filtered samples range between 12 and  $62 \mu g/L$ . All iron concentrations in unfiltered and filtered water samples are less than the  $90^{th}$  percentile Hanford Site background concentration of  $570 \mu g/L$ . Iron is not retained as a COPC for further evaluation in the FS.

Lead was detected in five of seven (71 percent) unfiltered groundwater samples. Lead concentrations in unfiltered samples range between 0.13 and 0.34  $\mu$ g/L. All lead results (detected concentrations and MDLs) are less than the state water quality standard (WAC 173-201A) of 2.1  $\mu$ g/L. Based on the results of this evaluation, lead is not retained as a COPC for further evaluation in the FS.

Manganese was detected in 8 of 30 (27 percent) of unfiltered and 5 of 21 samples (24 percent) of filtered groundwater samples. Manganese concentrations in unfiltered samples range between 9 and 41 and filtered groundwater samples range between 4.4 and 40  $\mu$ g/L. The action level for manganese of 384  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All manganese results (detected concentrations and MDLs) were less than the action level. The manganese concentration in one filtered sample is above than the 90<sup>th</sup> percentile Hanford Site background level of 39  $\mu$ g/L. Manganese is not retained as a COPC for further evaluation in the FS.

Nickel was detected in 10 of 30 (33 percent) unfiltered samples and 1 of 21 (4.8 percent) filtered groundwater samples. Nickel concentrations in unfiltered samples range between 0.21 and 7.8  $\mu$ g/L and the single measured concentration in a filtered sample was 6.9  $\mu$ g/L. Although all monitoring wells within the area were compared to the AWQC of 52  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. All nickel results (detected concentrations and MDLs) are less than the DWS. Except for one MDL for a filtered sample reported at 199-H4-12C, all nickel results for filtered samples (detected concentrations and MDLs) were less than the AWQC of 52  $\mu$ g/L. Based on the results of this evaluation, nickel is not retained as a COPC for further evaluation in the FS.

Selenium was not detected in any of the five unfiltered groundwater samples. All selenium MDLs are less than the AWQC of 5  $\mu$ g/L and the 90<sup>th</sup> percentile Hanford Site background level of 11  $\mu$ g/L. Selenium is not retained as a COPC for further evaluation in the FS.

Silver was not detected in any of the 30 unfiltered samples and was detected in one of 21 (4.8 percent) filtered samples. The single measured concentration in the filtered sample was 5.2  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. All MDLs (9 samples) reported by Method 200.8 were less than the state water quality standard. A total of 42 of 51 samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 4 and 11  $\mu$ g/L, all are greater than the AWQC and all are less than the DWS. The single silver detection was reported at 199-H4-15CS (5.2  $\mu$ g/L). This result was flagged with a "C" laboratory qualifier. The "C" qualifier indicates that the analyte was detected in both the sample and the associated QC blank, and the sample concentration was less than or equal to five times the blank concentration. Silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the AWQC. Based on these uncertainties, silver is retained as a COPC for further monitoring.

Thallium was not detected in any of the five unfiltered samples. The action level for thallium is  $0.5 \mu g/L$  and is based on the DWS goal. All MDL were less than the DWS goal and the  $90^{th}$  percentile Hanford Site background level of  $1.7 \mu g/L$ . Thallium is not retained as a COPC for further evaluation in the FS.

Uranium was detected in all 23 samples (100 percent) of the unfiltered samples. Filtered groundwater samples were not analyzed. All uranium results were less than the DWS. Uranium is not retained as a COPC for further evaluation in the FS.

Vanadium was detected in 29 of 30 (97 percent) unfiltered and all 21 (100 percent) filtered groundwater samples. All vanadium results (detected concentrations and single MDL) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was detected in 13 of 30 (43 percent) unfiltered and 5 of 21 (24 percent) filtered groundwater samples. Zinc concentrations in unfiltered samples range between 1.3 and 156  $\mu$ g/L and range between 4 and 87 in filtered groundwater samples. Although all monitoring wells within the area were compared to the state water quality standard of 91  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800  $\mu$ g/L. All zinc results (detected concentrations and MDLs) for unfiltered samples were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All zinc results (detected concentrations and MDLs) for filtered samples were less than the state water quality standard. Zinc is not retained as a COPC for further evaluation in the FS.

Data are also available for aluminum, barium, calcium, magnesium, potassium sodium, and strontium, which are not retained for further analysis. Aluminum concentrations are below the secondary MCL and the AWQC; calcium, magnesium, potassium, and sodium are essential nutrients; and the barium and strontium concentrations are below the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720) groundwater cleanup levels.

**Confined Aquifer Analytes—Horn Area.** The following subsections describe the analyte data that were available from completed wells and met the 7-year period criteria in the Horn, and include radionuclides, anions, and metals. The results presented in Table N-22 include all data collected during the specified period.

**Radionuclides.** Gross alpha and gross beta were identified as additional analytes in the 100-D/H SAP (DOE/RL-2009-40). Gross alpha and gross beta were analyzed in all three of the confined aquifer wells. Gross alpha was detected in 5 of 34 (15 percent) of the groundwater samples and gross beta was detected in 32 of 34 (94 percent) of the samples. Gross alpha was detected at concentrations ranging between 2 and 9.1 pCi/L, which are less than the DWS of 15 pCi/L. Gross beta was detected at concentrations ranging between 2.9 and 12 pCi/L. Gross beta concentrations are generally consistent with the presence of tritium and strontium-90. While the concentrations of strontium-90 were not analyzed, gross beta had a maximum value of 12 pCi/L; therefore, the presence of strontium-90 is not expected. Based on the results of this evaluation, gross alpha and gross beta are not retained as COPCs to be further evaluated in the FS.

Tritium was detected in 8 of 25 (32 percent) of the groundwater samples with concentrations ranging between 390 and 780 pCi/L. All results (detected concentrations and MDLs) are less than the DWS of 20,000 pCi/L. Tritium is not retained as a COPC for further evaluation in the FS.

**Anions.** Fluoride was detected in 21 of 24 (88 percent) of groundwater samples with concentrations ranging between 67  $\mu$ g/L and 371  $\mu$ g/L. All fluoride results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 960  $\mu$ g/L. Fluoride concentrations in unfiltered samples are also less than the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Based on the results of this evaluation, fluoride is not retained as a COPC for further evaluation in the FS.

Nitrate was detected in all 24 (100 percent) groundwater samples with concentrations ranging between 436  $\mu$ g/L and 18,300  $\mu$ g/L. All nitrate results (detected concentrations) were less than the DWS. Nitrate is not retained as a COPC in the confined aquifer for further evaluation in the FS.

Nitrite was detected in 5 of 24 (21 percent) of groundwater samples with concentrations ranging between 153  $\mu$ g/L and 267  $\mu$ g/L. All nitrite results (detected concentrations and MDLs) are less than the DWS. Nitrite concentrations in unfiltered samples are greater than the 90th percentile Hanford Site background level of 94  $\mu$ g/L. Based on the results of this evaluation, nitrite is not retained as a COPC for further evaluation in the FS.

Sulfate was detected in all 24 (100 percent) groundwater samples with concentrations ranging between 11,400  $\mu$ g/L and 56,000  $\mu$ g/L. All sulfate results are less than the secondary DWS. Based on the results of this evaluation, sulfate is not retained as a COPC for further evaluation in the FS.

Data are also available for other anions that are not retained for further analysis. There are no action levels for bromide or phosphate, and chloride concentrations are all below the AWQC.

**Metals.** Antimony was not detected in any of the 25 unfiltered samples or 25 filtered groundwater samples. All unfiltered and filtered samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 4 and 60  $\mu$ g/L (42 of 50 MDLs for unfiltered samples and filtered samples were greater than the DWS). Antimony MDLs reported by Method 6010 are not accurate at concentrations at or near the DWS. Based on these uncertainties, antimony is retained as a COPC for further monitoring.

Beryllium was not detected in any of the 25 unfiltered or filtered samples. All MDLs were less than or equal to the DWS. Beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was not detected in any of the unfiltered or filtered samples. All unfiltered and filtered samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 range between 0.45 and 4  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 0.25  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 5  $\mu$ g/L. All MDLs are greater than the AWQC and all MDLs are less than the DWS. Cadmium results reported by Method 6010 are not accurate at concentrations at or near the AWQC or the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on these uncertainties, cadmium is retained as a COPC for further monitoring.

Total chromium was detected in 9 of 25 (36 percent) of unfiltered samples and 8 of 25 (32 percent) of filtered groundwater samples. Chromium concentrations in unfiltered samples range between 3.6 and 70  $\mu$ g/L and filtered samples range between 3.1 and 70  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. All chromium results (detected concentrations and MDLs) are less than the DWS. Chromium concentrations in one filtered sample above the AWQC of 65  $\mu$ g/L was reported at well 699-97-48C. Chromium concentrations above the AWQC was reported in one of eight sampling rounds at Well 699-97-48C. Chromium concentrations are above the 90th percentile Hanford Site background level of 2.4  $\mu$ g/L. Chromium is retained as a COPC for further evaluation in the FS.

Cobalt was not detected in any of the 25 unfiltered samples and was detected in 1 of 25 filtered groundwater samples. The single cobalt detection was reported at 699-97-48C (5.9  $\mu$ g/L) which is greater than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4.8  $\mu$ g/L; all other cobalt results were reported as nondetects. All unfiltered and filtered samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 4 and 5  $\mu$ g/L (2 of 49 MDLs greater than the action level). Some of the cobalt MDLs reported by Method 6010 are not accurate at concentrations at or near the action level. Based on these uncertainties, cobalt is retained as a COPC for further monitoring.

Copper was detected in 3 of 25 unfiltered samples (12 percent) and 2 of 25 filtered groundwater samples (8 percent). All copper results (detected concentrations and MDLs) were less than the AWQC of 9  $\mu$ g/L but all detected concentrations were greater than the 90th percentile Hanford Site background level. Based on the results of this evaluation, copper is not retained as a COPC for further evaluation in the FS.

Cr(VI) was detected in 14 of 38 (37 percent) of unfiltered samples and 7 of 17 (41 percent) of filtered groundwater samples. Cr(VI) concentrations in unfiltered samples range between 3.7 and 63  $\mu$ g/L and concentrations in filtered samples range between 8 and 42  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the state surface water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L. Cr(VI) concentrations in filtered samples above the state surface water quality standard of 10  $\mu$ g/L were reported in all six sample rounds at 699-97-48C. Cr(VI) concentrations in unfiltered samples above the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level were reported in two of 13 sample rounds at 699-97-48C. Cr(VI) is retained as a COPC for further evaluation in the FS.

Iron was detected in 19 of 25 (76 percent) of unfiltered and 15 of 25 (60 percent) of filtered groundwater samples. All iron concentrations measured in filtered samples are less than the AWQC of 1,000  $\mu$ g/L. All iron concentrations measured in unfiltered samples are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200  $\mu$ g/L. Iron is not retained as a COPC for further evaluation in the FS.

Manganese was detected in 21 of 25 (84 percent) of unfiltered and 18 of 25 samples (72 percent) of filtered groundwater samples. Manganese concentrations in unfiltered samples range between 4.9 and  $602 \mu g/L$  and filtered groundwater samples range between 7.1 and 567  $\mu g/L$ . Manganese concentrations in unfiltered samples above the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level were reported in two of nine sample rounds at 699-97-45B. Manganese is not retained as a COPC for further evaluation in the FS.

Nickel was detected in 1 of 25 (4 percent) unfiltered samples and 1 of 25 (4 percent) filtered groundwater samples. All nickel results (detected concentrations and MDLs) are less than the AWQC of 52  $\mu$ g/L. Based on the results of this evaluation, nickel is not retained as a COPC for further evaluation in the FS.

Silver was not detected in any of the 25 unfiltered or filtered samples. All unfiltered and filtered samples were analyzed by Method 6010. MDLs for samples analyzed by Method 6010 ranged between 4 and 7  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the state water quality standard of 2.6  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. All MDLs are greater than the state water quality standard and all MDLs are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the state water quality standard. Based on these uncertainties, silver is retained as a COPC for further monitoring.

Vanadium was detected in 20 of 25 (80 percent) unfiltered and 20 of 25 (80 percent) filtered groundwater samples. All vanadium results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was detected in 11 of 25 (44 percent) unfiltered and 7 of 25 (28 percent) filtered groundwater samples. Zinc concentrations in unfiltered samples range between 4 and 121  $\mu$ g/L which are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800  $\mu$ g/L. Zinc concentrations in filtered samples range between 7.6 and 92  $\mu$ g/L in filtered groundwater samples. Zinc was detected above the state water quality standard in one filtered sample from 699-97-45B (92  $\mu$ g/L); all eight subsequent rounds were less than the state water quality standard. Zinc is not retained as a COPC for further evaluation in the FS.

Data are also available for barium, calcium, magnesium, potassium sodium, and strontium, which are not retained for further analysis. Calcium, magnesium, potassium, and sodium are essential nutrients, and the barium and strontium concentrations are below the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup levels.

Summary of the Confined Aquifer Groundwater Evaluation. Table 4-13 summarizes the outcome of the evaluation. Contaminants that warrant further evaluation in the FS include chromium and Cr(VI). Antimony, cadmium, cobalt, and silver are retained as COPCs for further monitoring based on uncertainties associated with the analytical method (infrequent detections or MDLs above the action level). In 100-D, Cr(VI) was carried to the FS based on a single detection above the surface water quality standard in one well location. In 100-H, total chromium and Cr(VI) are found in several locations along the river, without comparable concentrations in the unconfined aquifer above. Strontium-90 is also found at locations less than the DWS in the same locations as Cr(VI) at 100-H. Total chromium and Cr(VI) are found in one well within the Horn area.

	Area Evaluated				
Category	100-D	100-Н	Horn		
	Is retained	as a COPC			
Detected at levels above	Antimony*	Antimony*	Antimony*		
action level and background	Cadmium*	Cadmium*	Cadmium*		
	Hexavalent Chromium	Chromium	Chromium		
	Silver*	Cobalt*	Cobalt*		
	Zinc*	Hexavalent Chromium	Hexavalent Chromium		
		Silver*	Silver*		

Table 4-13. Summary of Confined Aguifer Evaluation

COPC = contaminant of potential concern

RD/RAWP = remedial design/remedial action work plan

# 4.4.1.4 Groundwater Evaluation for the Treatability Test Areas

Four treatability test areas were identified for evaluation in this section. The treatability test areas were evaluated to determine if the technologies achieved action levels; therefore, the analyte concentrations that are compared to action levels are those following treatment.

One in situ redox manipulation (ISRM) barrier test area is located within the larger 100-D Area plume and one is located in the 100-H Area plume. Additionally, two treatability tests were conducted within the

<sup>\*</sup> Note: Groundwater contaminants that do not warrant further evaluation in the FS, but have infrequent detections above an action level will be included in the RD/RAWP for continued monitoring at appropriate locations and frequency.

100-D Area: one treated groundwater with molasses and the second with emulsified vegetable oil. In total, 82 wells were identified to represent groundwater conditions within the ISRM of the 100-D Area: one well was identified to represent groundwater conditions within the ISRM of the 100-H Area; six wells were identified to represent groundwater conditions for the molasses treatability test area; and six wells were identified to represent groundwater conditions for the emulsified vegetable oil treatability test area. Groundwater concentrations from each of the areas were compared to the action levels described in Section 4.4.1.2. The historical COPCs identified for the 100-HR-3 groundwater OU are presented in Tables N-23 through N-26.

The nature and extent of contamination for groundwater in treatability test areas was based on the last seven years of data (samples collected between January 1, 2006 and December 31, 2012). The wells that were identified to represent groundwater conditions in each of the treatability test areas are listed in Table 4-14. Figure 4-68 provides the locations of the wells considered in this evaluation. Groundwater data for each of the treatability test areas were compiled and statistically analyzed and the results are presented in Appendix N (Tables N-23 through N-26). These tables present the summary statistics for each analyte where data were available from the completed well and met the 7-year period criteria. The tables also list the background concentrations in Hanford Site groundwater (*Hanford Site Background: Part 3, Groundwater Background* [DOE/RL-96-61]) where available, and the corresponding action level.

Table 4-14. Summary of Wells included in the Treatability Test Area Groundwater Evaluation

100-D ISRM Wells					
199-D3-2	199-D4-3	199-D4-50	199-D4-7 199-D4-70		
199-D3-3	199-D4-30	199-D4-51			
199-D3-4	199-D4-31	199-D4-52	199-D4-71		
199-D4-1	199-D4-32	199-D4-53	199-D4-72 199-D4-73 199-D4-74		
199-D4-10	199-D4-33	199-D4-54			
199-D4-11	199-D4-34	199-D4-55			
199-D4-12	199-D4-35	199-D4-56	199-D4-75		
199-D4-13	199-D4-36	199-D4-57	199-D4-76		
199-D4-14	199-D4-37	D4-37 199-D4-58			
199-D4-19	199-D4-4 199-D4-59		199-D4-78		
199-D4-2	199-D4-40	199-D4-6	199-D4-79		
199-D4-20	199-D4-41	199-D4-60	199-D4-8		
199-D4-21	199-D4-42	199-D4-61	199-D4-80		
199-D4-22	199-D4-43	199-D4-62	199-D4-81		
199-D4-23	199-D4-44	199-D4-63	199-D4-82		
199-D4-24	199-D4-45	199-D4-64	199-D4-84		

Table 4-14. Summary of Wells included in the Treatability Test Area Groundwater Evaluation

	100-D ISF	RM Wells			
199-D4-25	199-D4-46	199-D4-65	199-D4-9		
199-D4-26	199-D4-47	199-D4-66	199-D4-92		
199-D4-27	199-D4-48	199-D4-67	199-D4-93		
199-D4-28	199-D4-49	199-D4-68			
199-D4-29	199-D4-5	199-D4-69			
	100-H ISF	RM Wells			
199-H5-1A					
	<b>Biostimulation Treatability</b>	Test Area (Molasses) Wells			
199-D5-107	199-D5-110	199-D5-112	199-D5-113		
199-D5-109	199-D5-111	-			
Biostin	nulation Treatability Test Arc	ea (Emulsified Vegetable Oi	l) Wells		
199-D5-108	199-D5-115	199-D5-117	199-D5-118		
199-D5-114	199-D5-116				

ISRM = in situ redox manipulation

**100-D ISRM.** The 100-D ISRM area currently includes 82 wells that monitor the ISRM barrier that was installed to remediate a chromium groundwater plume in the 100-D Area by reducing Cr(VI) in the groundwater to Cr(III) through the injection of sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) into the aquifer, thus creating a chemically reduced environment. The first dithionite injection took place in September 1997, with four additional dithionite injections occurring in May through July 1998 (includes treatment injections into 199-D4-13, 199-D4-14, 199-D4-19, and 199-D4-7). During the fall of 1999, the treatability test area was extended by the treatment of well 199-D4-21.

Reduced treatment capacity was discovered in some of the treated wells; as a result an alternative technology was evaluated using micron-sized zero-valent iron (ZVI) polymer. This polymer was used to potentially mend the barrier and to eliminate the need of periodically injecting the ISRM wells with sodium dithionite. Well 199-D4-26 was identified as the injection well for the iron slurry, and wells 199-D4-92, 199-D4-93, 199-D4-25, and 199-D4-27 were nearby wells used to monitor the effects of the injection. The presence of the iron slurry in the treated wells used for the ISRM barrier created reducing conditions, increasing the concentrations of some metals and creating a matrix interference for some anions and metals. As a result of elevated concentrations or matrix interferences, groundwater samples were diluted and, because of the dilution and interference, some of the metals results were reported as nondetected concentrations with MDLs above the action level. Thus, some of the results for anions and metals are inconclusive.

Groundwater summary statistics for the ISRM within the 100-D Area are presented in Table N-23. As discussed previously, this data set represents groundwater data collected between January 2006 and December 2012.

**Radionuclides.** Gross alpha was detected in 8.6 percent of the unfiltered groundwater samples and gross beta was detected in 86 percent of the unfiltered samples. Gross alpha was detected at concentrations ranging between 1.2 and 4.2 pCi/L, all less than the DWS of 15 pCi/L Gross beta was detected at concentrations ranging between 3.4 and 220 pCi/L. Gross beta concentrations are consistent with the presence of tritium. Based on the results of this evaluation, gross alpha and gross beta are not identified as COPCs to be further evaluated in the FS.

Technetium-99 was detected in 2 of 8 (25 percent) of the unfiltered groundwater samples with concentrations ranging between 8.1 and 16 pCi/L. All results (detected concentrations and MDLs) were less than the DWS of 900 pCi/L. Based on the results of this evaluation, technetium-99 is not retained as a COPC for further evaluation in the FS.

Tritium was detected in 59 of 77 (77 percent) of the unfiltered groundwater samples with concentrations ranging between 260 and 28,500 pCi/L. Except for tritium results reported at well 199-D4-78, all tritium results (detected concentrations and MDLs) are less than or equal to the DWS of 20,000 pCi/L. Tritium was reported at 199-D4-78 with concentrations that range between 28,500 in 2006 decreasing to 3,400 pCi/L in 2012. Tritium concentrations have decayed to concentrations less than the DWS of 20,000 pCi/L. Based on the results of this evaluation, tritium is not retained as a COPC for further evaluation in the FS.

Cesium-137, cobalt-60, europium-152, europium-154, europium-155, and strontium-90 were not detected in any of the groundwater samples analyzed within the ISRM area. All MDLs were less than their respective DWSs.

**Anions.** Fluoride was detected in 242 of 422 (57 percent) of unfiltered groundwater samples with concentrations ranging between 26  $\mu$ g/L and 1,430  $\mu$ g/L. With the exception of fluoride results from well 199-D4-26 and 199-D4-93, all fluoride results are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 960  $\mu$ g/L and the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Four of 10 sample rounds for well 199-D4-26 report fluoride concentrations above background with concentrations ranging between 50 and 1,430  $\mu$ g/L. One of 27 sample rounds report fluoride concentrations above background at well 199-D4-93 with concentrations ranging between less than 150 and less than 1,500  $\mu$ g/L. As a result of matrix interferences, 44 of 180 samples required dilution and reported MDLs at concentrations greater than the action level. Based on the results of this evaluation, fluoride is retained as a COPC for further monitoring.

Nitrate was detected in 367 of 422 (87 percent) of the unfiltered groundwater samples with concentrations ranging between 93  $\mu$ g/L and 73,000  $\mu$ g/L. Nitrate was reported above the DWS in 10 of the 82 wells within the ISRM area including the following: 199-D4-20, 199-D4-22, 199-D4-25, 199-D4-26, 199-D4-27, 199-D4-31, 199-D4-36, and 199-D4-5. Based on the results of this evaluation, nitrate is retained as a COPC for further evaluation in the FS.

Nitrite was detected in 194 of 422 (46 percent) of unfiltered samples with concentrations ranging between 62 and 5,580  $\mu$ g/L. Nitrite was reported above the DWS in two of the 82 wells within the ISRM area including 199-D4-36 and 199-D4-62. One of 18 samples from well 199-D4-36 report nitrite concentrations above the DWS with concentrations ranging between less than 84 and 1,450  $\mu$ g/L. Two of 15 sample rounds for well 199-D4-62 report nitrite concentrations above the DWS with concentrations ranging between less than 125 and 5,580  $\mu$ g/L. Nitrite concentrations in unfiltered samples are also

greater than the  $90^{th}$  percentile Hanford Site background level of  $94 \mu g/L$ . Based on the results of this evaluation, nitrite is retained as a COPC for further evaluation in the FS.

Sulfate was detected in 537 of 542 (99 percent) of unfiltered samples with concentrations ranging between 7,740 and 590,000  $\mu$ g/L. Sulfate was reported above the secondary DWS in 11 of the 82 wells within the ISRM area including the following: 199-D4-1, 199-D4-19, 199-D4-23, 199-D4-4, 199-D4-5, 199-D4-6, 199-D4-62, 199-D4-78, 199-D4-13, 199-D4-7, and 199-D4-84. Based on the results of this evaluation, sulfate is retained as a COPC for further evaluation in the FS.

Metals. Antimony was detected in 12 of 175 unfiltered samples (6.9 percent) and 9 of 187 (4.8 percent) of the filtered groundwater samples. Antimony concentrations in unfiltered and filtered groundwater samples range between 5.1 and 73 μg/L. MDLs for all samples range between 0.3 and 76 μg/L. The action level for antimony is 6 μg/L based on the DWS and the  $90^{th}$  percentile Hanford Site background level is 55 μg/L. All unfiltered and filtered samples were analyzed by Method 6010 (311 of 341 MDLs were greater than the DWS). As discussed in previous sections, antimony results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the DWS or the Hanford Site background value. Based on the results of this evaluation, antimony is retained as a COPC for further monitoring.

Arsenic was detected in 159 of 165 (96 percent) of the unfiltered and 114 of 130 (88 percent) of the filtered groundwater samples. Arsenic concentrations range between 0.4 and 17  $\mu$ g/L in unfiltered and filtered groundwater samples. The action level for arsenic of 0.058  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Minimum, maximum, and 90th percentile concentrations for (filtered) background concentrations of arsenic are 0.5, 8.8, and 7.85  $\mu$ g/L, respectively. Arsenic was reported at concentrations higher than the maximum background level in four wells including 199-D4-25, 199-D4-1, 199-D4-7, and 199-D4-93. A total of five unfiltered samples were collected from 199-D4-25 with concentrations ranging between 5.6 and 11  $\mu$ g/L (two results greater than background). A total of seven unfiltered samples were collected from 199-D4-7 with concentrations ranging between 1.8 and 12  $\mu$ g/L (two results greater than background). A total of 15 unfiltered samples were collected from 199-D4-93 with concentrations ranging between 0.88 and 17  $\mu$ g/L (two results greater than background). The presence of arsenic in unfiltered samples is likely naturally occurring and supported by the infrequent reporting of concentrations outside the range of the 90th percentile Hanford Site background concentration. Based on the results of this evaluation, arsenic is not retained as a COPC for further evaluation in the FS.

Beryllium was not detected in any of the 173 unfiltered samples and was detected in 1 of 187 (0.5 percent) filtered groundwater samples. The single detection of beryllium (0.13  $\mu$ g/L) is less than the DWS and the 90<sup>th</sup> percentile Hanford Site background level of 2.3  $\mu$ g/L. Twenty of 359 MDLs (4.1 and 8  $\mu$ g/L) were reported at concentrations greater than the DWS. Based on the results of this evaluation, beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was detected in 18 of 213 (8.5 percent) of the unfiltered samples and in 1 of 187 (0.5 percent) of the filtered groundwater samples. Cadmium concentrations in unfiltered groundwater samples range between 0.1 and 5.9  $\mu$ g/L and the single detection in the filtered sample was 0.31  $\mu$ g/L. MDLs for all samples range between 0.1 and 8  $\mu$ g/L. Although all monitoring wells within this area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 5  $\mu$ g/L. A total of 348 of the 400 samples were analyzed by Method 6010. MDLs for results reported by Method 6010 range between 0.91 and 8  $\mu$ g/L; all are greater than the AWQC of 0.25  $\mu$ g/L and one is greater than the DWS. With the exception of one MDL and two samples with a "B" qualifier, all cadmium results (detected concentrations and MDLs) are less

than the DWS. As discussed in previous sections, cadmium results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the AWQC or the  $90^{th}$  percentile Hanford Site background level of  $0.92~\mu g/L$ . Based on the results of this evaluation, cadmium is retained as a COPC for further monitoring.

Chromium (total) was detected in 83 percent of the unfiltered and 73 percent of the filtered groundwater samples. Chromium (total) was reported above the AWQC of 65  $\mu$ g/L in 54 percent of the detected unfiltered results and 47 percent of the detected filtered results. Concentrations of unfiltered chromium (total) range between 3.5 and 1,020  $\mu$ g/L and filtered chromium (total) ranged between 3.2 and 992  $\mu$ g/L. All MDLs were less than the AWQC of 65  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the AWQC, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. Chromium is retained as a COPC for further evaluation in the FS.

Cobalt was detected in 55 of 177 (31 percent) of unfiltered samples and 42 of 187 (22 percent) of filtered groundwater samples. Cobalt concentrations in unfiltered and filtered groundwater samples range between 0.45 and 34  $\mu$ g/L. MDLs for all samples range between 4 and 8  $\mu$ g/L. The action level for cobalt of 4.8  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. A total of 348 of the 364 samples were analyzed by Method 6010. MDLs for results reported by Method 6010 range between 4 and 8  $\mu$ g/L; 32 of 348 MDLs are greater than the action level. All but one filtered and three unfiltered cobalt results reported by Method 6010 were either flagged with a "B" qualifier (47 of 77 results) or flagged with a "C" qualifier (30 of 77 results). Cobalt concentrations for unfiltered and filtered samples flagged with a "B" ranged between 4.1 and 21  $\mu$ g/L (40 of 47 results above action level). Cobalt concentrations for unfiltered and filtered samples flagged with a "C" ranged between 18 and 34  $\mu$ g/L (all results above action level). All cobalt results reported by Method 200.8 are less than the action level. As discussed in previous sections, cobalt results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the action level or the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation, cobalt is retained as a COPC for further monitoring.

Copper was detected in 70 of 213 (33 percent) of unfiltered samples and 36 of 187 (19 percent) of filtered groundwater samples. Copper concentrations in unfiltered samples range between 0.23 and 160 µg/L and filtered groundwater samples range between 0.22 and 22 µg/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 9 µg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640 µg/L. All copper results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All MDLs are less than the AWQC. All filtered copper concentrations analyzed by Method 601() (32 results) were flagged with either a "B" laboratory qualifier (16 of 32 results), a "C" laboratory qualifier (15 of 32 results), or a "BC" laboratory qualifier (1 of 32 results). Copper concentrations flagged with a "B" ranged between 2.8 and 22 μg/L (8 of 16 results above AWQC) and copper concentrations flagged with a "C" or "BC" ranged between 4.2 and 19 ug/L (11 of 16 results above AWOC). All filtered copper results reported by Method 200.8 are less than the AWQC. As discussed in previous sections, copper results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the AWQC or the 90th percentile Hamford Site background level of 0.81 µg/L. Based on the results of this evaluation, copper is retained as a COPC for further monitoring.

Cr(VI) was detected in 93 percent of the unfiltered and 72 percent of the filtered groundwater samples. Cr(VI) was reported above the state surface water quality standard of  $10 \mu g/L$  in 76 percent of the

detected unfiltered results and 76 percent of the detected filtered results. Although all monitoring wells within the area were compared to the state surface water quality standard value of  $10~\mu g/L$ , these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu g/L$ . Concentrations of filtered Cr(VI) ranged between 2 and 1,040  $\mu g/L$ . With the exception of 13 sample results, all MDLs were less than or equal to the state surface water quality standard of  $10~\mu g/L$ . Cr(VI) is retained as a COPC for further evaluation in the FS.

Iron was detected in 167 of 211 (79 percent) of unfiltered and 82 of 187 (44 percent) of filtered groundwater samples. Iron concentrations in unfiltered samples range between 14 and over 2,000,000 μg/L and range between 11 and 99,000 μg/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 1,000 μg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200 μg/L. Iron in unfiltered samples was reported above the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200 μg/L in four of the 82 wells within the ISRM area including the following: 199-D3-2, 199-D4-26, 199-D4-92, and 199-D4-93. Iron in filtered samples was reported above the AWQC in three of the 82 wells within the ISRM area including the following: 199-D3-2, 199-D4-92, and 199-D4-93. Well 199-D4-26 was the injection well for the ZVI slurry and the remaining wells were used to monitor the effects of the injection. The presence of elevated iron concentrations in the above wells is the result of reducing conditions created by the presence of the ZVI polymer. Based on the results of this evaluation, iron is retained as a COPC for further monitoring.

Lead was detected in 42 of 46 (91 percent) of unfiltered samples and 1 of 7 (14 percent) of filtered groundwater samples. Lead concentrations in unfiltered groundwater samples range between 0.26 and 22  $\mu$ g/L and the single detection in the filtered sample was 0.34  $\mu$ g/L. Although all monitoring wells within the ISRM area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 15  $\mu$ g/L. All MDLs were less than the state water quality criteria of 2.1  $\mu$ g/L. The single lead detection in the filtered sample was also less than the state water quality standard. Lead concentrations in unfiltered samples were reported above the DWS in well 199-D4-25. Lead concentrations were above the DWS in four of five samples collected at 199-D4-25 with concentrations ranging between 14 and 22  $\mu$ g/L. Well 199-D4-25 is a well that was used to monitor the effects of the iron slurry injection. Lead concentrations in filtered samples are less than the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation, lead is retained as a COPC for further monitoring.

Manganese was detected in 138 of 213 (65 percent) of unfiltered and 94 of 187 (50 percent) of filtered groundwater samples. Manganese concentrations range between 4 and 2,910  $\mu$ g/L in unfiltered samples and range between 4.1 and 530  $\mu$ g/L in filtered groundwater samples. The action level for manganese of 384  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Manganese was reported above the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level in three of the 82 wells within the ISRM area including the following: 199-D4-26, 199-D4-92, and 199-D4-93. Well 199-D4-26 was the injection well for the ZVI slurry and the remaining wells were used to monitor the effects of the injection. The presence of elevated iron concentrations in the above wells is the result of reducing conditions created by the presence of the ZVI polymer. Based on the results of this evaluation, manganese is retained as a COPC for further monitoring.

Mercury was not detected in any of the six filtered or unfiltered groundwater samples analyzed. The analytical method cannot attain the AWQC of 0.012 µg/L; therefore, nondetected concentrations are

reported at the EQL of  $0.5 \mu g/L$  identified in the 100-D/H SAP (DOE/RL-2009-40). All mercury MDLs were less than the EQL of  $0.5 \mu g/L$ . Based on the results of this evaluation, mercury is not retained as a COPC for further evaluation in the FS.

Nickel was detected at a number of wells and aquifer tubes in the vicinity of the 100-D ISRM area at levels higher than the AWQC of 52 µg/L and the DWS of 100 µg/L. Figure 4-69 shows all the wells and aquifer tubes in the 100-D Area that showed observed nickel concentrations in filtered groundwater samples above 52 µg/L. The observed trends are consistent with release of nickel (and other metals) from native aquifer sediments as a result of the reducing conditions associated with the sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) injections. To illustrate these trends, sulfate concentrations are also shown for each of the wells with elevated nickel concentrations. Most of the wells show a release of nickel in filtered groundwater samples that followed the same trends of sulfate concentrations in the aguifer at the wells and aguifer tubes shown with black font. As an example, well 199-D4-5 shows sulfate concentrations peaking at 1,500 mg/L on 3/4/2003. The peak nickel concentration value of 294 µg/L at this well was observed on 12/1/2003. Since then nickel (and sulfate) concentrations have been declining; with the most recent nickel measurement at this location at 5.1 µg/L, which is well below the AWQC. As another example, at aquifer tube DD-43-3 sulfate and nickel concentrations have been increasing and decreasing in tandem since 2007. At this aguifer tube, nickel concentrations measured at low river stage (December and January) have been in the range of 4 to 10 μg/L since 2011; well below the AWQC. Since 2012, no nickel concentrations above the AWQC have been measured at any of these wells or aquifer tubes.

The second group of wells in Figure 4-69 is shown with green font (wells 199-D4-20, 199-D4-85, and 199-D4-15). At these locations the correlation between nickel and sulfate concentrations is not evident. There is no question that these wells are within the reductive zone as a result of the ISRM (as evidenced by the measured sulfate concentrations. Factors contributing to this apparent lack of correlation are: (1) high detection limits such as the  $66.5 \mu g/L$  value reported at well 199-D4-20 as a detection limit (because of sample dilution) and  $66.5 \mu g/L$  detection limit at well 199-D4-15, (2) laboratory or sampling contamination reported as C flag (value similar to that measured in the trip blank sample) such as the 27.5  $\mu g/L$  concentration reported at 199-D4-85 on 11/6/2007. For all wells in this group, detected nickel concentrations have been well below the AWQC since 2009.

The last group of wells in Figure 4-69 is shown with purple font (wells 199-D5-36, 199-D5-38, 199-D5-107, 199-D5-108, and 199-D5-115). These wells are located upstream from the ISRM wells but could be impacted by ISRM during high river stages, when groundwater gradients are inland. At these locations, nickel concentrations measured in filtered groundwater are not well correlated with sulfate concentrations, perhaps due to different transport pathways from the ISRM wells towards these locations but all measured nickel concentrations at all of these wells have been steadily declining. The apparent increases at wells 199-D5-36 and 199-D5-38 are due to high detection limits for few samples. Similar to the other two groups, detected nickel concentrations have been well below the AWQC since 2011.

In conclusion, nickel concentrations have been observed in response to the ISRM at wells and aquifer tubes. Some of these concentrations were above the AWQC and the DWS but concentrations have been steadily declining and no observed nickel concentrations have been reported above the AWQC since 2011. Based on the results of this evaluation, nickel is not retained as a COPC for further evaluation in the FS.

Selenium was detected in 5 of 7 (71 percent) of unfiltered and 6 of 7 (86 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater area were compared to the AWQC of 5  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 50  $\mu$ g/L. Selenium concentrations in unfiltered samples range

between 0.76 and 2.2  $\mu$ g/L and filtered samples range between 0.72 and 2.6  $\mu$ g/L. All selenium results (detected concentrations and MDLs) are less than the AWQC. All selenium concentrations are also less than or equal to the 90<sup>th</sup> percentile Hanford Site background level of 11  $\mu$ g/L. Based on the results of this evaluation, selenium is not retained as a COPC for further evaluation in the FS.

Silver was detected in 32 of 175 (18 percent) of unfiltered and 22 of 187 (12 percent) of filtered groundwater samples. Silver concentrations in unfiltered samples range between 6 and 134 µg/L and filtered samples range between 0.29 and 32 µg/L. Although all monitoring wells within the groundwater area were compared to the state water quality standard (WAC 173-201A) of 2.6 µg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80 µg/L. All MDLs reported by Method 6010 were greater than the state water quality standard and all were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All silver concentrations in filtered samples analyzed by Method 6010 (21 results) were greater than the state water quality standard; all of the results were either flagged with a "B" laboratory qualifier (4 of 21 results) or flagged with a "BC" or "C" laboratory qualifier (17 of 21 results). Silver concentrations flagged with a "B" ranged between 6.7 and 14 µg/L and silver concentrations flagged with a "C" ranged between 6.6 and 32 μg/L. Silver concentrations in unfiltered samples were reported at concentrations greater than the groundwater cleanup level at well 199-D4-36 (134 µg/L) and well 199-D4-78 (97 μg/L); these are the only silver results reported at these wells (these results are unflagged). All silver results reported by Method 200.8 are less than the state water quality standard. As discussed in previous sections, silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the state water quality standard or the 90th percentile Hanford Site background level of 5.3 µg/L. Based on the results of this evaluation, silver is retained as a COPC for further monitoring.

Thallium was not detected in any of the six unfiltered samples and was detected in 1 of 6 (17 percent) of filtered groundwater samples. The single thallium detection was  $0.32 \mu g/L$ , which was less than the DWS goal of  $0.5 \mu g/L$ . All MDLs were also less than the DWS goal. Based on the results of this evaluation, thallium is not retained as a COPC for further evaluation in the FS.

Uranium was detected in 143 of 145 (99 percent) of unfiltered and both filtered groundwater samples. Uranium concentrations in unfiltered samples range between 0.1 and 5.7  $\mu$ g/L and filtered samples range between 1.6 and 3.6  $\mu$ g/L. All uranium results (detected concentrations and MDLs) were less than the DWS of 30  $\mu$ g/L. Uranium concentrations in unfiltered and filtered samples are below the 90<sup>th</sup> percentile Hanford Site background level of 9.9  $\mu$ g/L. Based on the results of this evaluation, uranium is not retained as a COPC for further evaluation in the FS.

Vanadium was detected in 80 of 175 (46 percent) unfiltered samples and 70 of 187 (37 percent) of filtered groundwater samples. All vanadium results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Vanadium concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 12  $\mu$ g/L. Based on the results of this evaluation, vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was detected in 123 of 213 (56 percent) unfiltered samples and 71 of 187 (38 percent) filtered groundwater samples. Zinc concentrations in unfiltered samples range between 1.2 and 960  $\mu$ g/L and range between 4.4 and 499  $\mu$ g/L in filtered samples. Although all monitoring wells within the groundwater area were compared to the state water quality standard of 91  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA

("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 μg/L. All zinc results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 μg/L. All MDLs for filtered samples were less than the state water quality standard. Zinc concentrations in filtered samples greater than the state water quality standard were reported in six of the 82 wells within ISRM including the following: 199-D3-2, 199-D4-20, 199-D4-23, 188-D4-84, 199-D4-92, and 199-D4-93. Each of the wells listed above were used to monitor the effects of the injection. The presence of elevated zinc concentrations in the above wells is the result of reducing conditions created by the presence of the ZVI polymer. Based on the results of this evaluation, zinc is retained as a COPC for further monitoring.

**Summary of the 100-D ISRM Area Groundwater Evaluation.** Table 4-15 summarizes the outcome of the analysis. Contaminants that warrant further evaluation in the FS are chromium (total), Cr(VI), and nitrate. Groundwater contaminants that do not warrant further evaluation in the FS but have infrequent detections above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency.

Table 4-15. Summary of 100-D ISRM Area Contaminant Evaluation

Category	Constituent				
Retained as a COPC					
Contaminant of potential concern* (contaminants that warrant further evaluation in FS)	Chromium, Cr(VI), nitrate				
Retained for I	Monitoring				
Detected at levels above action level and background	Antimony, cadmium, cobalt, copper, fluoride, iron, lead, manganese, nitrite, silver, sulfate, zinc				
Not Retained as a COPC					
Detected in groundwater but below action level, EQL, or background concentrations	Arsenic, beryllium, gross alpha, nickel, selenium, technetium-99, thallium, tritium, uranium, vanadium				
Not detected in groundwater	Cesium-137, cobalt-60, europium-152. europium-154, europium-155, mercury, strontium-90				

<sup>\*</sup> Based on evaluation of data collected January 2006 through December 2012.

COPC = contaminant of potential concern

EQL = estimated quantitation limit

FS = feasibility study

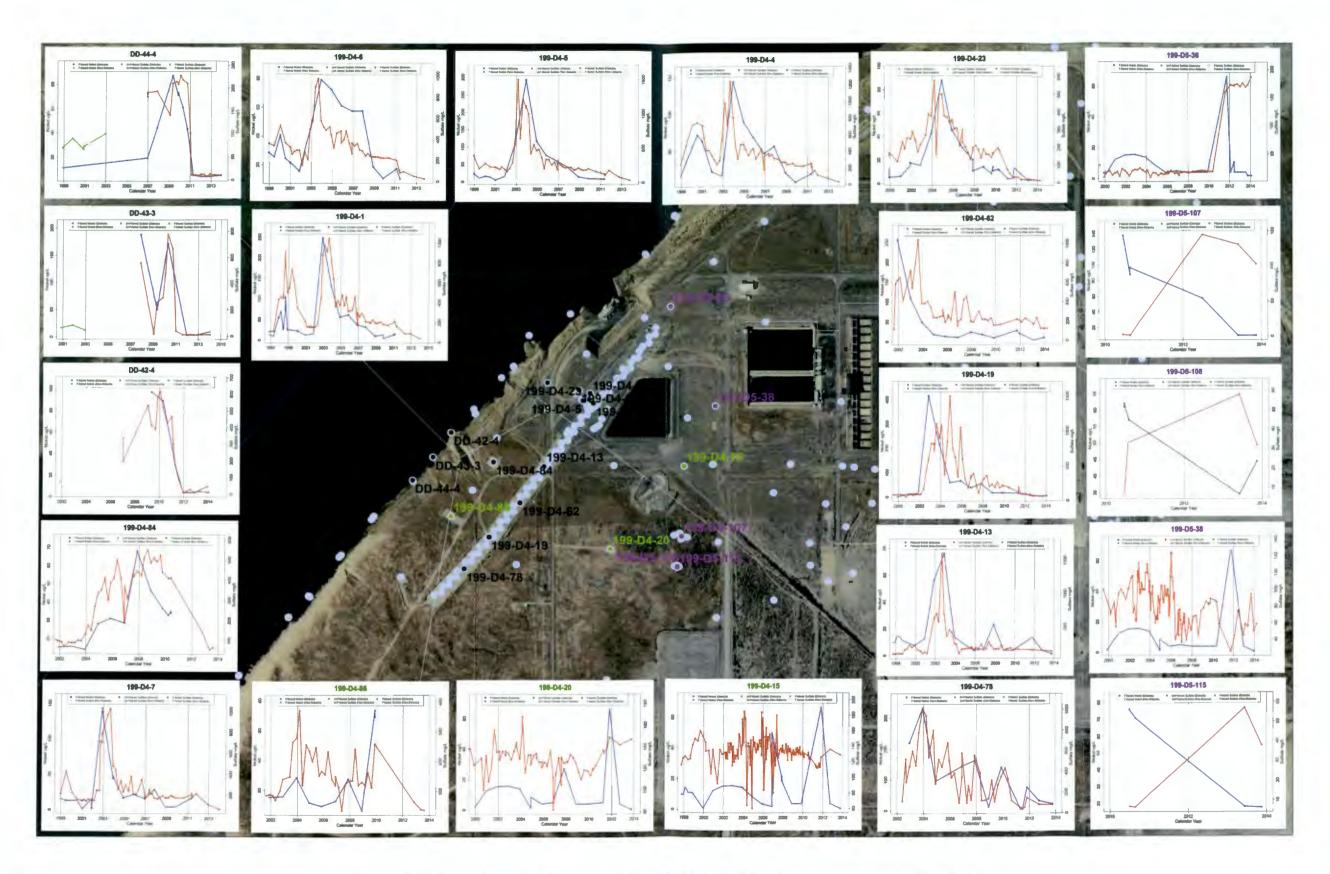


Figure 4-69. Wells and Aquifer Tubes in Vicinity of 100-D ISRM with Nickel Concentrations Greater Than AWQC

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**100-H ISRM**. The 100-H ISRM area currently includes one well that monitors the ISRM barrier that was installed to remediate a chromium groundwater plume in the 100-H Area by reducing the Cr(VI) in the groundwater to Cr(III) through the injection of sodium dithionite into the aquifer, thus creating a chemically reduced environment. The main dithionite injection took place in September 1995. During the period after the injection, 13 wells were used to monitor the performance of the barrier. However, only one well (199-H5-1A) is currently being monitored for groundwater contamination.

Groundwater summary statistics for the ISRM within the 100-H Area are presented in Table N-24. As discussed previously, this data set represents groundwater data collected between January 2006 and December 2012. These data are from one well that monitors the vicinity of the ISRM area.

**Radionuclides.** Gross beta was detected in all four of the unfiltered samples with concentrations ranging between 4 and 14 pCi/L. Gross beta concentrations are consistent with the presence of tritium. Based on the results of this evaluation and the groundwater risk assessment presented in Section 6.3, gross beta is not identified as a COPC to be further evaluated in the FS.

Tritium was detected in four of the unfiltered groundwater samples with concentrations ranging between 2,800 and 4,500 pCi/L. All tritium results are less than the DWS of 20,000 pCi/L. Based on the results of this evaluation, tritium is not retained as a COPC for further evaluation in the FS.

Cesium-137, cobalt-60, europium-152, europium-154, europium-155, gross alpha, strontium-90, and technetium-99 were not detected in any of the groundwater samples analyzed within the ISRM area. All MDLs were less than their respective DWSs.

Volatile Organic Compounds. Chloroform was detected in one of three (33 percent) of unfiltered groundwater samples with the single detection reported at 0.44  $\mu$ g/L. All chloroform results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 1.4  $\mu$ g/L. Based on the results of this evaluation, chloroform is not retained as a COPC for further evaluation in the FS.

Benzene, carbon tetrachloride, trichloroethene, and vinyl chloride were not detected in any of the groundwater samples analyzed within the ISRM area.

**Anions.** Fluoride was detected in 5 of 7 (71 percent) of unfiltered groundwater samples with concentrations ranging between 91  $\mu$ g/L and 220  $\mu$ g/L. All fluoride results are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 960  $\mu$ g/L and the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Based on the results of this evaluation, fluoride is not retained as a COPC for further evaluation in the FS.

Nitrate was detected in all seven (100 percent) of the unfiltered groundwater samples with concentrations ranging between 27,500  $\mu$ g/L and 35,700  $\mu$ g/L. All nitrate results (detected concentrations and MDLs) were less than the DWS of 45,000  $\mu$ g/L. Based on the results of this evaluation, nitrate is not retained as a COPC for further evaluation in the FS.

Nitrite was detected in 3 of 6 (50 percent) of unfiltered samples with concentrations ranging between 214 and 1,380  $\mu$ g/L. All nitrite results (detected concentrations and MDLs) were less than the DWS of 3,300  $\mu$ g/L. Nitrite concentrations in unfiltered samples are greater than the 90<sup>th</sup> percentile Hanford Site background level of 94  $\mu$ g/L. Based on the results of this evaluation, nitrite is not retained as a COPC for further evaluation in the FS.

Sulfate was detected in all seven (100 percent) unfiltered samples with concentrations ranging between 44,300 and  $97,900 \mu g/L$ . All sulfate results (detected concentrations and MDLs) were less than the

secondary DWS of 250,000  $\mu$ g/L. Based on the results of this evaluation, sulfate is not retained as a COPC for further evaluation in the FS.

Metals. Antimony was detected in 3 of 4 unfiltered samples (75 percent) and 3 of 5 (60 percent) of the filtered groundwater samples. Antimony concentrations in unfiltered and filtered groundwater samples range between 0.65 and 0.81 μg/L (these results were reported by Method 200.8). MDLs for three samples range between 32 and 45 μg/L (these results were reported by Method 6010). The action level for antimony is 6 μg/L based on the DWS and the 90<sup>th</sup> percentile Hanford Site background level is 55 μg/L. All detected concentrations are less than the DWS. As discussed in previous sections, antimony results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the DWS or the Hanford Site background value. Because antimony concentrations from Method 200.8 indicate it is not present above the DWS, antimony is not retained as a COPC and warrants further evaluation in the FS.

Arsenic was detected in all three of the unfiltered and filtered groundwater samples with concentrations ranging between 1.9 and 2.4  $\mu$ g/L in unfiltered and filtered groundwater samples. The action level for arsenic of 0.058  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Minimum, maximum, and 90<sup>th</sup> percentile concentrations for (filtered) background concentrations of arsenic are 0.5, 8.8, and 7.85  $\mu$ g/L, respectively. All arsenic results are less than the 90<sup>th</sup> percentile Hanford Site background concentration. Based on the results of this evaluation, arsenic is not retained as a COPC for further evaluation in the FS.

Beryllium was not detected in any of the four unfiltered samples and was detected in 1 of 5 (20 percent) filtered groundwater samples. The single detection of beryllium (0.16  $\mu$ g/L) is less than the DWS of 4  $\mu$ g/L and the 90<sup>th</sup> percentile Hanford Site background level of 2.3  $\mu$ g/L. All MDLs are less than the DWS. Based on the results of this evaluation, beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was not detected in any of the four unfiltered samples or five filtered groundwater samples. MDLs for all samples range between 0.2 and 4  $\mu$ g/L. Although all monitoring wells within this area were compared to the AWQC of 0.25  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 5  $\mu$ g/L. Six of nine samples were analyzed by trace methods (Method 200.8) and reported with MDLs of 0.2  $\mu$ g/L (all less than the AWQC and DWS). Three of the nine samples were analyzed by Method 6010 and reported with MDLs of 2.3 and 4  $\mu$ g/L (all greater than the AWQC and less than the DWS). As discussed in previous sections, cadmium results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the AWQC or the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation, cadmium is not retained as a COPC for further evaluation in the FS.

Chromium was detected in all four unfiltered samples (100 percent) and in four of five filtered groundwater samples (80 percent). Chromium concentrations in unfiltered and filtered samples range between 4.1 and 25  $\mu$ g/L. Although all monitoring wells within this area were compared to the AWQC of 65  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. All chromium results (detected concentrations and MDLs) were less than the AWQC and the DWS. Based on the results of this evaluation, chromium is not retained as a COPC for further evaluation in the FS.

Cobalt was detected in 1 of 4 (25 percent) of unfiltered samples and 1 of 5 (20 percent) of filtered groundwater samples. Cobalt concentrations in unfiltered and filtered groundwater samples range between 0.14 and 0.19  $\mu$ g/L. The action level for cobalt of 4.8  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Six of nine samples were analyzed by trace methods (Method 200.8) and were reported with MDLs of 0.1  $\mu$ g/L (all less than

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the action level). Two detected concentrations were reported by Method 200.8; however, both were flagged with a "C" laboratory qualifier. Three of the nine samples were analyzed by Method 6010 and reported with MDLs of 4 and 5  $\mu$ g/L (two of three less than the action level). Because cobalt concentrations from Method 200.8 indicate it is not present above the action level, cobalt is not retained as a COPC and warrants further evaluation in the FS.

Copper was detected in 3 of 4 (75 percent) of unfiltered samples and 2 of 5 (40 percent) of filtered groundwater samples. Copper concentrations in unfiltered and filtered samples range between 0.20 and 0.65  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 9  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640  $\mu$ g/L. All copper results (detected concentrations and MDLs) are less than the AWQC and the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All filtered copper results are less than the 90<sup>th</sup> percentile Hanford Site background level of 0.81  $\mu$ g/L. Based on the results of this evaluation, copper is not retained as a COPC for further evaluation in the FS.

Cr(VI) was detected in all 15 (100 percent) of unfiltered samples and 8 of 9 (89 percent) of filtered groundwater samples. Cr(VI) concentrations in unfiltered and filtered samples range between 6 and 39  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the state surface water quality standard of 10  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L. All Cr(VI) results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. However, six of nine Cr(VI) results in filtered samples are greater than the state surface water quality standard of 10  $\mu$ g/L. Based on the results of this evaluation, Cr(VI) is retained as a COPC for further evaluation in the FS.

Iron was detected in all four (100 percent) of unfiltered and all five (100 percent) of filtered groundwater samples. Iron concentrations in unfiltered and filtered samples range between 25 and 110  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 1,000  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200  $\mu$ g/L. All iron results (detected concentrations and MDLs) were less than the AWQC and the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Based on the results of this evaluation, iron is not retained as a COPC for further evaluation in the FS.

Lead was not detected in any of the three unfiltered or filtered samples. Although all monitoring wells within the ISRM area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of  $15 \,\mu\text{g/L}$ . All MDLs were less than the state water quality standard of  $2.1 \,\mu\text{g/L}$  and the DWS. Lead concentrations in filtered samples are less than the  $90^{th}$  percentile Hanford Site background level of  $0.92 \,\mu\text{g/L}$ . Based on the results of this evaluation, lead is not retained as a COPC for further evaluation in the FS.

Manganese was not detected in any of the unfiltered or filtered groundwater samples. The action level for manganese of 384  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All MDLs were less than the action level. Based on the results of this evaluation, manganese is not retained as a COPC for further evaluation in the FS.

Mercury was not detected in any of the filtered or unfiltered groundwater samples analyzed. The analytical method cannot attain the AWQC of  $0.012~\mu g/L$ ; therefore, nondetected concentrations are reported at the EQL of  $0.5~\mu g/L$  identified in the 100-D/H SAP (DOE/RL-2009-40). All mercury MDLs were less than the EQL of  $0.5~\mu g/L$ . Based on the results of this evaluation, mercury is not retained as a COPC for further evaluation in the FS.

Nickel was not detected in any of the unfiltered or filtered groundwater samples. Although all monitoring wells within the area were compared to the AWQC of  $52 \mu g/L$ , these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of  $100 \mu g/L$ . All MDLs were less than the AWQC and the DWS. Based on the results of this evaluation, nickel is not retained as a COPC for further evaluation in the FS.

Selenium was detected in all three (100 percent) of unfiltered and all three (100 percent) of filtered groundwater samples. Although all monitoring wells within the groundwater area were compared to the AWQC of 5  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 50  $\mu$ g/L. All detected concentrations are less than the AWQC, DWS, and the 90<sup>th</sup> percentile Hanford Site background level of 11  $\mu$ g/L. Based on the results of this evaluation, selenium is not retained as a COPC for further evaluation in the FS.

Silver was detected in 1 of 4 (25 percent) of unfiltered and 1 of 5 (20 percent) of filtered groundwater samples. Silver concentrations in unfiltered and filtered samples range between 0.4 and 1  $\mu$ g/L. Although all monitoring wells within the area were compared to the state water quality standard (WAC 173-201A) of 2.6  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Four of six samples analyzed by trace methods (Method 200.8) were reported with MDLs of 0.2  $\mu$ g/L (all less than the state water quality standard). Three of the nine samples were analyzed by Method 6010 and reported MDLs of 5 and 5.2  $\mu$ g/L (all greater than the state water quality standard). All MDLs were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. As discussed in previous sections, silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the state water quality standard or the 90<sup>th</sup> percentile Hanford Site background level of 5.3  $\mu$ g/L. Because silver concentrations from Method 200.8 indicate it is not present above the state water quality standard, silver is not retained as a COPC and warrants further evaluation in the FS.

Thallium was not detected in any of the three unfiltered samples and was detected in 1 of 3 (33 percent) of filtered groundwater samples. The single thallium detection was 0.1  $\mu$ g/L, which is less than the DWS goal of 0.5  $\mu$ g/L. All MDLs are also less than the DWS goal. Based on the results of this evaluation, thallium is not retained as a COPC for further evaluation in the FS.

Uranium was detected in all three (100 percent) of unfiltered and the single filtered groundwater samples. Uranium concentrations in unfiltered and filtered samples range between 1.3 and 1.5  $\mu$ g/L. All uranium results (detected concentrations) were less than the DWS of 30  $\mu$ g/L. Uranium concentrations in unfiltered and filtered samples are below the 90<sup>th</sup> percentile Hanford Site background level of 9.9  $\mu$ g/L. Based on the results of this evaluation, uranium is not retained as a COPC for further evaluation in the FS.

Vanadium was not detected in any of the four unfiltered samples and was detected in 2 of 5 (40 percent) of filtered groundwater samples. All vanadium results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Vanadium concentrations in all samples are below the 90<sup>th</sup> percentile Hanford Site background level of 12  $\mu$ g/L. Based on the results of this evaluation, vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was detected in 2 of 4 (50 percent) unfiltered samples and 3 of 5 (60 percent) filtered groundwater samples. Zinc concentrations in unfiltered samples range between 6.8 and 13  $\mu$ g/L and range between 6.4 and 15  $\mu$ g/L in filtered samples. Although all monitoring wells within the groundwater area were compared to the state water quality standard, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800  $\mu$ g/L. All zinc results (detected concentrations and MDLs) are less than the state water quality standard and the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Zinc concentrations in all samples are below the 90<sup>th</sup> percentile Hanford Site background level of 22  $\mu$ g/L. Based on the results of this evaluation, zinc is not retained as a COPC for further evaluation in the FS.

Summary of the 100-H ISRM Area Groundwater Evaluation. Table 4-16 summarizes the outcome of the analysis. The only contaminant that warrants further evaluation in the FS is Cr(VI). Groundwater contaminants that do not warrant further evaluation in the FS, but have infrequent detections above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency.

Table 4-16. Summary of 100-H ISRM Area Contaminant Evaluation

Table 4-10. Guillinary of 100-11 lottin Area Containinant Evaluation					
Category	Constituent				
Retained as a COPC					
Contaminant of potential concern* (contaminants that warrant further evaluation in FS)	Hexavalent chromium				
Retained for I	Monitoring				
Detected at levels above action level and background	None				
Not Retained	as a COPC				
Detected in groundwater but below action level, EQL, or background concentrations	Antimony, arsenic, beryllium, chloroform, chromium cobalt, copper, fluoride, iron, nitrate, nitrite, selenium silver, sulfate, thallium, tritium, uranium, vanadium, zinc				
Not detected in groundwater	Benzene, cadmium, carbon tetrachloride, cesium-13' cobalt-60, europium-152. europium-154, europium-155, gross alpha, lead, manganese, mercury, nickel, strontium-90, technetium-99, trichloroethene, vinyl chloride				

<sup>\*</sup> Based on evaluation of data collected January 2006 through December 2012.

COPC = contaminant of potential concern

EQL = estimated quantitation limit

FS = feasibility study

### **Biostimulation Treatability Test Using Molasses**

The 100-D in situ biostimulation test using molasses currently includes three wells that monitor the groundwater conditions in the vicinity of this treatability test. The purpose of the in situ biostimulation test was to create a biological barrier. This process is performed through amending the aquifer with a

substrate (molasses) that induces growth and/or activity of indigenous bacteria for the purpose of inducing reduction of chromate, nitrate, and oxygen to remove these compounds from the groundwater. Molasses was selected as the soluble substrate to create the in situ biobarrier. Molasses was injected into well 199-D5-107 and five wells were selected to monitor the performance of the treatability test (199-D5-109, 199-D5-111, 199-D5-112, and 199-D5-113). The molasses was injected in September 2007 and the performance of the treatability test was subsequently monitored for two years.

Groundwater summary statistics for the biostimulation treatability test area are presented in Table N-25. As discussed previously, this data set represents groundwater data collected between January 2006 and December 2012. These data are from three wells that monitor the treatability test area.

**Volatile Organic Compounds.** 1,1-Dichlorobenzene, benzene, carbon tetrachloride, chloroform, trichloroethene, and vinyl chloride were not detected in any of the groundwater samples analyzed within the treatability test area.

**Anions.** Fluoride was detected in 6 of 8 (75 percent) of unfiltered groundwater samples with concentrations ranging between 79  $\mu$ g/L and 364  $\mu$ g/L. All fluoride results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 960  $\mu$ g/L and the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Based on the results of this evaluation, fluoride is not retained as a COPC for further evaluation in the FS.

Nitrate was detected in 1 of 8 (12.5 percent) of the unfiltered groundwater samples with a single detected concentration of 14,400  $\mu$ g/L. All nitrate results (detected concentrations and MDLs) were less than the DWS of 45,000  $\mu$ g/L and less than background. Based on the results of this evaluation, nitrate is not retained as a COPC for further evaluation in the FS.

Nitrite was detected in 1 of 8 (12.5 percent) of the unfiltered groundwater samples with a single detected concentration of 992  $\mu$ g/L. All nitrite results (detected concentrations and MDLs) were less than the DWS of 3,300  $\mu$ g/L. Based on the results of this evaluation, nitrite is not retained as a COPC for further evaluation in the FS.

Sulfate was detected in all eight (100 percent) of unfiltered samples with concentrations ranging between 1,340 and 145,000  $\mu$ g/L. All detected concentrations were less than the secondary DWS of 250,000  $\mu$ g/L. Based on the results of this evaluation, sulfate is not retained as a COPC for further evaluation in the FS.

**Metals.** Antimony was not detected in any of the eight unfiltered samples or filtered groundwater samples analyzed. The action level for antimony is 6  $\mu$ g/L based on the DWS. All samples were analyzed by Method 6010 and MDLs ranged between 36 and 47  $\mu$ g/L. All MDLs are greater than the DWS but are less than the 90<sup>th</sup> percentile Hanford Site background level of 55  $\mu$ g/L. As discussed in previous sections, antimony results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the DWS or the Hanford Site background value. Based on the results of this evaluation, antimony is retained as a COPC for further monitoring.

Beryllium was not detected in any of the eight unfiltered samples or filtered groundwater samples analyzed. The action level for beryllium of 4  $\mu$ g/L is based on the DWS. All MDLs are less than or equal to the DWS but are greater than the 90<sup>th</sup> percentile Hanford Site background level of 2.3  $\mu$ g/L. Based on the results of this evaluation, beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was not detected in any of the eight unfiltered samples or filtered groundwater samples analyzed. Although all monitoring wells within this area were compared to the AWQC of 0.25  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland

would need to meet the DWS of 5  $\mu$ g/L. MDLs for all samples were reported as 4  $\mu$ g/L. MDLs are less than the DWS but are greater than the AWQC and greater than the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. As discussed in previous sections, cadmium results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the AWQC or the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation, cadmium is retained as a COPC for further monitoring.

Chromium was detected in 1 of 8 unfiltered samples (12.5 percent) and in 1 of 8 filtered groundwater samples (12.5 percent). Chromium concentrations in unfiltered and filtered samples range between 14 and 15  $\mu$ g/L. Although all monitoring wells within this area were compared to the AWQC of 65  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. All chromium results (detected concentrations and MDLs) were less than the AWQC and the DWS. Based on the results of this evaluation, chromium is not retained as a COPC for further evaluation in the FS.

Cobalt was detected in 5 of 8 (63 percent) of unfiltered samples and 5 of 8 (63 percent) of filtered groundwater samples. Cobalt concentrations in unfiltered and filtered groundwater samples range between 4 and 24  $\mu$ g/L. The action level for cobalt of 4.8  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All samples were analyzed by Method 6010. All filtered samples and four of five unfiltered samples report cobalt concentrations greater than the action level and all MDLs are less than the action level. As discussed in previous sections, cobalt results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the action level or the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation, cobalt is retained as a COPC for further monitoring.

Copper was detected in 5 of 8 (63 percent) of unfiltered samples and 3 of 8 (38 percent) of filtered groundwater samples. Copper concentrations in unfiltered samples range between 5 and 52 µg/L and concentrations in filtered groundwater samples range between 4 and 17 µg/L. MDLs for all samples range between 4 and 5 µg/L. Although all monitoring wells within the test area were compared to the AWOC of 9 μg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640 µg/L. All copper results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All MDLs are less than the AWQC. All detected filtered copper concentrations analyzed by Method 6010 (3 results) were flagged with a "B" laboratory qualifier with concentrations ranging between 4 and 16 µg/L (1 of 3 results above AWQC). Copper was detected once in filtered samples above the AWQC in well 199-D5-107 at a concentration above the AWQC (17 µg/L); however, two previous rounds were less than the AWQC. As discussed in previous sections, copper results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the AWQC or the 90th percentile Hanford Site background level of 0.81 µg/L. Based on the results of this evaluation, copper is not retained as a COPC for further evaluation in the FS.

Cr(VI) was not detected in any of the eight unfiltered samples and was detected in 1 of 7 (14 percent) of filtered groundwater samples. The single detected Cr(VI) concentration was 4.8  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the state surface water quality standard of 10  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L. Eight of 14 MDLs are greater than the state surface water quality standard as a result of dilution required for analysis. Four of 14 MDLs were greater than the 2007 MTCA

("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Based on the results of this evaluation, Cr(VI) is retained as a COPC for further evaluation in the FS.

Iron was detected in all eight unfiltered and filtered groundwater samples analyzed. Iron concentrations in unfiltered samples range between 558 and 24,500  $\mu$ g/L and in filtered samples range between 405 and 24,500  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 1,000  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200  $\mu$ g/L. Iron was reported once above the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200  $\mu$ g/L at well 199-D5-109 (24,500  $\mu$ g/L); however, two subsequent sample rounds were less than the groundwater cleanup level (558 and 1,330  $\mu$ g/L). Iron was reported above the AWQC in all three wells. The presence of elevated iron concentrations in the above wells is the result of reducing conditions created by the presence of the soluble substrate (molasses). Based on the results of this evaluation, iron is retained as a COPC for further monitoring.

Manganese was detected in all eight unfiltered and filtered groundwater samples analyzed. Manganese concentrations in unfiltered and filtered samples range between 5,190 and 26,700  $\mu$ g/L. The action level for manganese of 384  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All manganese concentrations are greater than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The presence of elevated manganese concentrations in the above wells is the result of reducing conditions created by the presence of the soluble substrate. Based on the results of this evaluation, manganese is retained as a COPC for further monitoring.

Mercury was not detected in the single filtered or unfiltered groundwater sample analyzed. The analytical method cannot attain the AWQC of  $0.012~\mu g/L$ ; therefore, nondetected concentrations are reported at the EQL of  $0.5~\mu g/L$  identified in the 100-D/H SAP (DOE/RL-2009-40). Both mercury MDLs were less than the EQL of  $0.5~\mu g/L$ . Based on the results of this evaluation, mercury is not retained as a COPC for further evaluation in the FS.

Nickel was detected in all eight unfiltered and filtered groundwater samples analyzed. Nickel concentrations in unfiltered samples range between 9 and 143  $\mu$ g/L and filtered groundwater samples range between 5 and 138  $\mu$ g/L. Although all monitoring wells within the area were compared to the AWQC of 52  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. Nickel was detected once in an unfiltered sample from well 199-D5-107 (143  $\mu$ g/L) at a concentration greater than the DWS, all other reported concentrations are less than the DWS. All three reported nickel concentrations from filtered samples collected from well 199-D5-107 were greater than the AWQC. Nickel concentrations from the other two wells were less than the AWQC. Based on the results of this evaluation, nickel is retained as a COPC for further monitoring.

Silver was detected in 1 of 8 (12.5 percent) of unfiltered and 1 of 8 (12.5 percent) of filtered groundwater samples. The single detection of silver in the unfiltered sample was 7.6 µg/L and the single detection of silver in the filtered sample was 15 µg/L. Although all monitoring wells within the groundwater area were compared to the state water quality standard (WAC 173-201A) of 2.6 µg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80 µg/L. All silver results (detected concentrations and MDLs) were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All silver results from filtered

samples (detected concentration and MDLs) were greater than the state water quality standard. All samples were analyzed by Method 6010. As discussed in previous sections, silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the state water quality standard or the  $90^{th}$  percentile Hanford Site background level of  $5.3~\mu g/L$ . Based on the results of this evaluation, silver is retained as a COPC for further monitoring.

Vanadium was detected in 5 of 8 (63 percent) unfiltered samples and 6 of 8 (75 percent) of filtered groundwater samples. Vanadium concentrations in unfiltered and filtered samples range between 11 and 87  $\mu$ g/L. Vanadium was reported above the action level at well 199-D5-109; however, both results were flagged with a "C" laboratory qualifier. All remaining vanadium results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Vanadium concentrations in filtered samples are above the 90<sup>th</sup> percentile Hanford Site background level of 12  $\mu$ g/L. Based on the results of this evaluation, vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was detected in 3 of 8 (38 percent) unfiltered samples and 1 of 8 (12.5 percent) filtered groundwater samples. Zinc concentrations in unfiltered samples range between 7 and 12 μg/L and the single detection of zinc in the filtered sample measured 10 μg/L. Although all monitoring wells within the groundwater area were compared to the state water quality standard of 91 μg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 μg/L. All zinc results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800 μg/L and the state water quality standard. All zinc concentrations are less than the 90<sup>th</sup> percentile Hanford Site background level of 22 μg/L. Based on the results of this evaluation, zinc is not retained as a COPC for further evaluation in the FS.

Arsenic, lead, selenium, thallium, and uranium were not analyzed in any of the samples collected from this treatability test area.

Summary of the 100-D Biostimulation Treatability Area Using Molasses Groundwater Evaluation. Table 4-17 summarizes the outcome of the analysis. The only contaminant that warrants further evaluation in the FS is Cr(VI). Groundwater contaminants that do not warrant further evaluation in the FS, but have infrequent detections above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency.

Table 4-17. Summary of 100-D Biostimulation Treatability Test Area Using Molasses Contaminant Evaluation

Category	Constituent					
Retained as a COPC						
Contaminant of potential concern* (contaminants that warrant further evaluation in FS)	Cr(VI)					
Retained for	r Monitoring					
Detected at levels above action level and background	Antimony, cadmium, cobalt, iron, manganese, nicke silver					

Table 4-17. Summary of 100-D Biostimulation Treatability Test Area Using Molasses Contaminant Evaluation

Category	Constituent			
Not Retained as a COPC				
Detected in groundwater but below action level, EQL, or background concentrations	Chromium, copper, fluoride, nitrate, nitrite, selenium, sulfate, vanadium, zinc			
Not detected in groundwater	1,1-Dichloroethene, benzene, beryllium, carbon tetrachloride, chloroform, mercury, trichloroethene, vinyl chloride			

<sup>\*</sup> Based on evaluation of data collected January 2006 through December 2012.

COPC = contaminant of potential concern

EQL = estimated quantitation limit

FS = feasibility study

### Biostimulation Treatability Test using Emulsified Vegetable Oil

The 100-D in situ biostimulation test using emulsified oil currently includes three wells that monitor the groundwater conditions in the vicinity of this treatability test. The purpose of the in situ biostimulation test is to create a biological barrier. This process is performed through amending the aquifer with a substrate (vegetable oil) that induces growth and/or activity of indigenous bacteria for the purpose of inducing reduction of chromate, nitrate, and oxygen to remove these compounds from the groundwater. Soybean oil emulsion was selected as the immiscible substrate to create the in situ biobarrier. Emulsified oil was injected into well 199-D5-108 and five wells were selected to monitor the performance of the treatability test (199-D5-114, 199-D5-115, 199-D5-116, 199-D5-117, and 199-D5-118). The emulsified oil was injected in August 2008 and the performance of the treatability test was subsequently monitored for two years.

Groundwater summary statistics for the biostimulation treatability test within the 100-D Area are presented in Table N-26. As discussed previously, this data set represents groundwater data collected between January 2006 and December 2012. These data are from three wells that monitor the treatability test area.

**Volatile Organic Compounds.** 1,1-Dichloroethene, benzene, carbon tetrachloride, chloroform, trichloroethene, and vinyl chloride were not detected in any of the groundwater samples analyzed within the treatability test area.

**Anions.** Fluoride was detected in 1 of 7 (14 percent) of unfiltered groundwater samples with a single measured concentration of 219  $\mu$ g/L. All fluoride results (detected concentrations) are less than and all MDLs are greater than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 960  $\mu$ g/L. All samples required dilution due to the presence of matrix interferences. The single detection is less than the 90th percentile Hanford Site background level of 1,047  $\mu$ g/L. Based on the results of this evaluation, fluoride is not retained as a COPC for further evaluation in the FS.

Nitrate was not detected in any of the seven unfiltered groundwater samples. With the exception of one MDL (70,800  $\mu$ g/L), all nitrate MDLs were less than the DWS of 45,000  $\mu$ g/L. All samples required

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dilution due to the presence of matrix interferences. Based on the results of this evaluation, nitrate is not retained as a COPC for further evaluation in the FS.

Nitrite was not detected in any of the seven unfiltered groundwater samples. Three of seven MDLs (5,910 to 29,900  $\mu$ g/L) were greater than the DWS, the remaining four nitrite MDLs were less than the DWS of 3,300  $\mu$ g/L. All samples required dilution due to the presence of matrix interferences. Based on the results of this evaluation, nitrite is not retained as a COPC for further evaluation in the FS.

Sulfate was detected in 4 of 7 (57 percent) of the unfiltered samples with concentrations ranging between 6,210 and 13,800  $\mu$ g/L. All sulfate results (detected concentrations and MDLs) were less than the secondary DWS of 250,000  $\mu$ g/L. Based on the results of this evaluation, sulfate is not retained as a COPC for further evaluation in the FS.

**Metals.** Antimony was not detected in any of the seven unfiltered or filtered groundwater samples analyzed. The action level for antimony is 6  $\mu$ g/L based on the DWS. All samples were analyzed by Method 6010 and MDLs ranged between 38 and 47  $\mu$ g/L. All MDLs are greater than the DWS but are less than the 90<sup>th</sup> percentile Hanford Site background level of 55  $\mu$ g/L. As discussed in previous sections, antimony results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations at or near the DWS or the Hanford Site background value. Based on the results of this evaluation, antimony is retained as a COPC for further monitoring.

Beryllium was not detected in any of the seven unfiltered or filtered groundwater samples analyzed. The action level for beryllium of 4  $\mu$ g/L is based on the DWS. All MDLs are less than or equal to the DWS but are greater than the 90<sup>th</sup> percentile Hanford Site background level of 2.3  $\mu$ g/L. Based on the results of this evaluation, beryllium is not retained as a COPC for further evaluation in the FS.

Cadmium was not detected in any of the seven unfiltered or filtered groundwater samples analyzed. Although all monitoring wells within this area were compared to the AWQC of 0.25  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 5  $\mu$ g/L. MDLs for all samples were reported as 4  $\mu$ g/L. MDLs are less than the DWS but are greater than the AWQC and greater than the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. As discussed in previous sections, cadmium results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the AWQC or the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation, cadmium is retained as a COPC for further monitoring.

Chromium was not detected in any of the seven unfiltered samples or filtered groundwater samples analyzed. Although all monitoring wells within this area were compared to the AWQC of 65  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. All MDLs were less than the AWQC and the DWS. Based on the results of this evaluation, chromium is not retained as a COPC for further evaluation in the FS.

Cobalt was detected in 5 of 7 (71 percent) of unfiltered samples and 6 of 7 (86 percent) of filtered groundwater samples. Cobalt concentrations in unfiltered and filtered groundwater samples range between 4 and 94  $\mu$ g/L. MDLs for all samples are reported as 4  $\mu$ g/L. The action level for cobalt of 4.8  $\mu$ g/L is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All samples were analyzed by Method 6010. All but one of the measured concentrations in unfiltered and filtered samples are greater than the action level. As discussed in previous sections, cobalt results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the action level or the 90<sup>th</sup> percentile Hanford Site background level of 0.92  $\mu$ g/L. Based on the results of this evaluation, cobalt is retained as a COPC for further monitoring.

Copper was detected in 1 of 7 (14 percent) of unfiltered samples and was not detected in any of the seven filtered groundwater samples. The single detected concentration from an unfiltered sample measured 4.8 µg/L. MDLs for all samples range between 4 and 5 µg/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 9 µg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 640 µg/L. All copper results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level and the AWQC. The single detected copper concentration is above the 90<sup>th</sup> percentile Hanford Site background level of 0.81 µg/L. Based on the results of this evaluation, copper is not retained as a COPC for further evaluation in the FS.

Cr(VI) was detected in 5 of 7 unfiltered samples (71 percent) and was detected in 5 of 7 (71 percent) of filtered groundwater samples. Cr(VI) concentrations in unfiltered samples range between 2 and 11  $\mu$ g/L and range between 2 and 16  $\mu$ g/L in filtered samples. Although all monitoring wells within the groundwater area were compared to the state surface water quality standard of 10  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 48  $\mu$ g/L. All Cr(VI) results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. Cr(VI) was detected in both the unfiltered (11  $\mu$ g/L) and filtered (16  $\mu$ g/L) samples collected from well 199-D5-114 in March 2010. All remaining Cr(VI) results (detected concentrations and MDLs) were less than the state surface water quality standard. Based on the results of this evaluation, Cr(VI) is retained as a COPC for further evaluation in the FS.

Iron was detected in all seven unfiltered and filtered groundwater samples analyzed. Iron concentrations in unfiltered samples range between 1,640 and over 34,500 µg/L and range between 56 and 27,400 µg/L. Although all monitoring wells within the groundwater area were compared to the AWQC of 1,000 µg/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 11,200 µg/L. Iron was reported at concentrations above the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level in 5 of 7 filtered samples. Iron was reported above the AWQC in all three wells (199-D5-108, 199-D5-114, and 199-D5-115). The presence of elevated iron concentrations in the above wells is the result of reducing conditions created by the presence of the immiscible substrate (vegetable oil). Based on the results of this evaluation, iron is retained as a COPC for further monitoring.

Manganese was detected in all seven unfiltered and filtered groundwater samples analyzed. Manganese concentrations in unfiltered and filtered samples range between 10,900 and 36,200  $\mu g/L$ . The action level for manganese of 384  $\mu g/L$  is based on the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All manganese concentrations are greater than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. The presence of elevated manganese concentrations in the above wells is the result of reducing conditions created by the presence of the soluble substrate. Based on the results of this evaluation, manganese is retained as a COPC for further monitoring.

Mercury was not detected in the single filtered or unfiltered groundwater sample analyzed. The analytical method cannot attain the AWQC of  $0.012~\mu g/L$ ; therefore, nondetected concentrations are reported at the EQL of  $0.5~\mu g/L$  identified in the 100-D/H SAP (DOE/RL-2009-40). Both mercury MDLs were less than the EQL of  $0.5~\mu g/L$ . Based on the results of this evaluation, mercury is not retained as a COPC for further evaluation in the FS.

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Nickel was detected in 4 of 7 (57 percent) unfiltered samples and in 4 of 7 (57 percent) filtered groundwater samples analyzed. Nickel concentrations in unfiltered samples range between 58 and 69  $\mu$ g/L and filtered groundwater samples range between 57 and 76  $\mu$ g/L. Although all monitoring wells within the area were compared to the AWQC of 52  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the DWS of 100  $\mu$ g/L. All nickel results (detected concentrations and MDLs) were less than the DWS. All filtered nickel concentrations from well 199-D5-108 and 199-D5-115 were greater than the AWQC. All MDLs were less than the AWQC. Based on the results of this evaluation, nickel is retained as a COPC for further evaluation in the FS.

Silver was detected in 1 of 7 (14 percent) of unfiltered and 1 of 7 (14 percent) of filtered groundwater samples. The single detection of silver in the unfiltered sample was 5  $\mu$ g/L and the single detection of silver in the filtered sample was 7  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the state water quality standard (WAC 173-201A) of 2.6  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. All silver results (detected concentrations and MDLs) were less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level. All silver results from filtered samples (detected concentration and MDLs) were greater than the state water quality standard. All samples were analyzed by Method 6010. As discussed in previous sections, silver results (detected concentrations and MDLs) reported by Method 6010 are not accurate at concentrations near the state water quality standard or the 90<sup>th</sup> percentile Hanford Site background level of 5.3  $\mu$ g/L. Based on the results of this evaluation, silver is retained as a COPC for further monitoring.

Vanadium was detected in 1 of 7 (14 percent) unfiltered samples and was not detected in any of the seven filtered groundwater samples. The single detection of vanadium was 17  $\mu$ g/L. All vanadium results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 80  $\mu$ g/L. Vanadium concentrations in the single unfiltered sample and all MDLs are above or equal to the 90<sup>th</sup> percentile Hanford Site background level of 12  $\mu$ g/L. Based on the results of this evaluation, vanadium is not retained as a COPC for further evaluation in the FS.

Zinc was detected in 4 of 7 (57 percent) unfiltered samples and 4 of 7 (57 percent) filtered groundwater samples. Zinc concentrations in unfiltered and filtered samples range between 7 and 11  $\mu$ g/L. Although all monitoring wells within the groundwater area were compared to the state water quality standard of 91  $\mu$ g/L, these standards only apply for groundwater where it enters the Columbia River. Wells located inland would need to meet the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800  $\mu$ g/L. All zinc results (detected concentrations and MDLs) are less than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) groundwater cleanup level of 4,800  $\mu$ g/L and the state water quality standard. All zinc concentrations are less than the 90<sup>th</sup> percentile Hanford Site background level of 22  $\mu$ g/L. Based on the results of this evaluation, zinc is not retained as a COPC for further evaluation in the FS.

Arsenic, lead, selenium, thallium, and uranium were not analyzed in any of the samples collected from this treatability test area.

Summary of the 100-D Biostimulation Treatability Area Using Emulsified Vegetable Oil Groundwater Evaluation. Table 4-18 summarizes the outcome of the analysis. The only contaminant that warrants further evaluation in the FS is Cr(VI). Groundwater contaminants that do not warrant further evaluation in

the FS but have infrequent detections above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency.

Table 4-18. Summary of 100-D Biostimulation Treatability Test Area Using Emulsified Vegetable Oil Contaminant Evaluation

Category	Constituent				
Retained as a COPC					
Contaminant of potential concern* (contaminants that warrant further evaluation in FS)	Cr(VI)				
Retained for	Monitoring				
Detected at levels above action level and background	Antimony, cadmium, cobalt, iron, manganese, nickel, silver				
Not Retained	as a COPC				
Detected in groundwater but below action level, EQL, or background concentrations	Chromium, copper, fluoride, sulfate, vanadium, zinc				
Not detected in groundwater	1,1-Dichloroethene, benzene, beryllium, carbon tetrachloride, chloroform, chromium, mercury, nitrate nitrite, trichloroethene, vinyl chloride				

<sup>\*</sup> Based on evaluation of data collected January 2006 through December 2012.

COPC = contaminant of potential concern

EQL = estimated quantitation limit

FS = feasibility study

### 4.5 Distribution of Contaminants

Data were collected to better describe the nature and extent of contamination in the various stratigraphic units and enhance the understanding of the plumes. Analytical data from groundwater monitoring wells, remediation wells, and RPO wells were included in the evaluation. The 100-D/H Work Plan (DOE/RL-2008-46-ADD1), Section 4.8, identified the following data needs associated with obtaining a better understanding of the nature and extent of contamination in groundwater.

Data Need No. 5: Define the extent of groundwater contamination above cleanup standards in select areas of the unconfined aquifer. These data are needed to verify that the area southwest of the ISRM barrier was clean of contamination while the two new aquifer tubes at 100-H (C7649 and C7650) were installed to determine the extent of contamination between the 116-H-7 Retention Basins and the river.

To address this data gap, four new aquifer tubes and seven new wells were installed at 100-D and two new aquifer tubes and five new wells were installed at 100-H (Table 2-1). Sample locations are presented on Figures 2-1 and 2-2.

Data Need No. 7: Collect physical and hydrogeologic parameters from soil samples to support the determination of contaminant fate and transport beneath the unconfined aquifer. 100-D: Only one well (199-D8-54B) had been installed in the RUM in 100-D, in an area of relatively low concentrations in the

unconfined aquifer in the north chromium plume. Cr(VI) has been detected in the well above water quality standards. At 100-H, groundwater contaminant concentrations remain above the aquatic and DWSs in wells completed beneath the unconfined aquifer. Additional contaminant and hydrogeologic information is needed in the RUM to evaluate potential adverse impacts of groundwater discharging from the RUM through seeps and upwelling in the bottom of the river. Additional soil samples locations were selected to address spatial variability of hydraulic properties of the RUM. To address this data gap, additional wells were installed into the RUM, and soil and groundwater samples were collected at the locations shown on Figure 2-1 and Figure 2-2. Five wells were drilled into the RUM: 199-D5-134 (C7624, Well R4), 199-D5-141 (C7625, Well R5), 199-H2-1 (C7631, Well R3), 199-H3-9 (C7639, Well R1), and 199-H3-10 (C7640, Well R2). These wells were screened in the first water-bearing unit within the RUM. Water quality data include hydraulic conductivity testing (including slug tests and permeameter testing), temperature, pH, oxidation-reduction potential, dissolved oxygen, and turbidity, which were collected during sampling, well development, and slug tests. Analytical data from samples collected during drilling are presented in conjunction with the discussions of the specific contaminants. The vertical distribution of Cr(VI) is presented in Section 4.5.2, and includes analytical samples collected from lower units within the RUM.

Data Need No. 10: Collect soil and water samples from the following units: (1) vadose zone, (2) deep vadose zone, (3) rewetted zone, (4) unconfined aquifer, (5) above the RUM, and (6) within the RUM. These data are needed to evaluate alternative CSM components regarding whether groundwater contamination is from vadose zone sources (in areas of past handling and storage of high concentration sodium dichromate and in the periodically wetted zone), within the unconfined aquifer, above the RUM Unit, or within the RUM Unit and diffusing to the unconfined aquifer.

To address this data gap, soil and groundwater samples were collected at the locations shown on Figure 2-1 and Figure 2-2.

Groundwater data at 100-D were collected from seven unconfined aquifer wells, two wells drilled into the RUM, two boreholes converted to wells, three boreholes during drilling, and four aquifer tubes. At 100-H, groundwater data were collected from five unconfined aquifer wells, three wells drilled into the RUM, three boreholes converted to wells, two boreholes during drilling, and two aquifer tubes (Table 2-3). These 17 new monitoring wells and 6 aquifer tubes were installed to address Data Needs 5, 10, and 13 (Chapter 2).

Boreholes C7852, C7857, C7860, C7861, and C7863 were originally intended as temporary borings to collect soil samples and grab groundwater samples. Because of lithologic conditions that prohibited the collection of grab groundwater samples, the borings were converted to temporary Monitoring Wells 199-D8-101, 199-D5-142, 199-H4-84, 199-H4-83, and 199-H3-11, respectively. Five wells were drilled into the RUM: 199-D5-134 (C7624, Well R4), 199-D5-141 (C7625, Well R5), 199-H2-1 (C7631, Well R3), 199-H3-9 (C7639, Well R1), and 199-H3-10 (C7640, Well R2). These wells were screened in the first water-bearing unit within the RUM. Water quality data including conductivity, temperature, pH, oxidation-reduction potential, dissolved oxygen, and turbidity were collected during sampling, well development, and slug tests. Analytical data from samples collected during drilling are presented in conjunction with the discussions of the specific contaminants.

The following sections describe the nature and extent of Cr(VI), nitrate, strontium-90, and other contaminants in groundwater. Contaminants are discussed in order of the size of the footprint of the groundwater plume (aerial extent) exceeding the applicable standards as shown. Table 4-19 summarizes information on these plume areas.

Table 4-19. Approximate Areal Extent of 100-D/H Plumes for 2009 and 2011

Contaminant	Cı	r(VI)	C	Cr(VI)		Nitrate		Strontium-90	
Standard	10 μg/L	) μg/L 48 μg/L		45,000 μ	45,000 μg/L		8 pCi/L		
Area	in km <sup>2</sup> (mi <sup>2</sup> )		in km² (mi²)		in km² (r	in km² (mi²)		in km² (mi²)	
Year	2009	2011	2009	2011	2009	2011	2009	2011	
100-D	3.9 (1.5)	2.12 (0.82)	2.7 (1.0)	1.0 (0.38)	1.5 (0.57)	1.12 (0.43)	0.0 (0.0)	0.03 (0.01)	
100-Н	2.7 (1.0)	0.8 (0.31)	1.0 (0.38)	0.05 (0.02)	0.03 (0.01)	0.12 (0.05)	0.2 (0.09)	0.09 (0.03)	
Horn Area	13 (4.8)	4.34 (1.68)	4.7 (1.8)	0.74 (0.29)	0.0 (0.0)	0.21 (0.08)	0.0 (0.0)	0.0 (0.0)	
Total	19 (7.4)	7.26 (2.80)	8.3 (3.2)	1.78 (0.69)	1.5 (0.58)	1.44 (0.56)	0.2 (0.09)	0.12 (0.04)	

a. "Water Quality Standards for Surface Waters of the State of Washington" (WAC 173-201A). This standard only applies to groundwater that discharges to surface water at the interface.

Additional analytes discussed include those evaluated in the FS, based on the spatial and temporal analysis, as well as other analytes with detections.

#### 4.5.1 Hexavalent Chromium

Cr(VI) is present in groundwater at 100-D, 100-H, and across the Horn between the two reactor areas. Currently, Cr(VI) is primarily found within the unconfined aquifer of 100-D/H, with concentrations above 10  $\mu$ g/L present in the first water-bearing unit of the RUM at 100-H. The total footprint of the plume areas exceeding the 10  $\mu$ g/L state surface water quality standard, which applies to areas that discharge to surface water, is approximately 19 km² (7.4 mi²). The total footprint of the plume areas exceeding 48  $\mu$ g/L MTCA (WAC 173-340) DWS, which applies to the whole plume, is approximately 8.3 km² (3.2 mi²). The highest Cr(VI) concentrations in 100-D/H are located west of the 105-DR Reactor, commonly referred to as the southern 100-D plume "hot spot." Concentrations in the Horn and 100-H are significantly lower, often below 100  $\mu$ g/L. The Cr(VI) contamination in the Horn area groundwater, and to some degree in 100-H, is believed to have originated in 100-D and migrated east with groundwater flow. The spread of Cr(VI) across the Horn likely occurred during 105-D and 105-DR reactor operations, when the groundwater mound associated with the retention basins and cooling water effluent trenches was at its greatest extent.

A contributor to groundwater contamination at 100-D/H was the infiltration test at the 116-DR-1&2 Trench. The large volume of cooling water discharged to the 116-DR-1&2 Trench infiltrated the vadose zone, reaching the water table and expanding the groundwater mound already present from normal reactor operations. This created high hydraulic head conditions, forcing the water to migrate from the Ringold Formation unit E at 100-D into the Hanford formation of the Horn. Across the Horn, the geology transitions from Ringold Formation unit E to the Hanford formation dominating in the aquifer. Moving eastward toward 100-H, Hanford formation material dominates the unconfined aquifer, with smaller

b. "Model Toxics Control Act—Cleanup" (WAC 173-340(4)(b)(iii)).

c. "National Primary Drinking Water Regulations," "Maximum Contaminant Levels for Inorganic Contaminants" (40 CFR 141.62) (modified, 10,000 µg/L × 1/0.226).

d. "National Primary Drinking Water Regulations," "Maximum Contaminant Levels for Radionuclides" (40 CFR 141.66).

pockets of Ringold Formation unit E present (see Figure 3-9). In general, groundwater flow will follow the path of least resistance. This means that groundwater moving across the Horn would tend to remain in the Hanford formation, where there is less resistance to water flow. In addition, the groundwater mound would not migrate easily to the far northern portion of the Horn, where the aquifer is also present in the Hanford formation, because of the restricted flow caused by thin aquifer in that area (see Figure 3-8).

#### 4.5.1.1 100-D Area

The unconfined aquifer of the 100-D southern plume has the highest Cr(VI) concentrations in 100-D/H, with a maximum value of 69,700  $\mu$ g/L (Well 199-D5-122). In contrast, the concentrations across the Horn are consistently below 100  $\mu$ g/L and concentrations in 100-H are below 2,000  $\mu$ g/L. The highest concentration in the northern plume at 100-D was 2,310  $\mu$ g/L in well 199-D5-125, reported in June 2010. Monitoring Well 199-D5-122, which is located in the hot spot of the southern plume, has had levels over 60,000  $\mu$ g/L reported in January, April, and August of 2010. Concentrations in this well have declined in response to the operation of the DX pump-and-treat system, which started in December 2010, and ongoing waste site remediation activities which is removing vadose zone source material at the 100-D-100 waste site. As more wells have been installed at 100-D, the confidence in the plume location has improved. The area of highest concentrations in the southern plume (Well 199-D5-122) remains located in a central area near waste site 100-D-100 and 100-D-12. Figure 4-70 shows the waste sites associated with sodium dichromate use and disposal. These waste sites are potential source areas for the associated Cr(VI) groundwater plumes.

In the northern plume, the highest Cr(VI) concentrations are located at Well 199-D5-125. Cr(VI) concentrations in northern plume monitoring wells (199-D5-14, 199-D5-15, 199-D5-16, 199-D5-125, and 199-D5-126) have generally increased or remained relatively stable. Because waste site remediation is ongoing in 100-D, sources may remain in the vadose zone that are contributing to the groundwater plume. Potential source areas for the northern plume were investigated in 2009 (*Report on Investigation of Hexavalent Chromium Source in the Northern 100-D Area* [DOE/RL-2010-40]). Results indicated that the closest waste site that could be a source for the northern plume (100-D-104) is located approximately 250 m (820 ft) from the highest groundwater concentrations, making it an unlikely candidate. Ongoing excavation at 100-D-104 has indicated that Cr(VI) may extend to groundwater in that area.

Interim remedial actions have or will address source areas associated with the northern plume. These waste sites include 116-D-1A and 116-D-1B cribs (300 m [985 ft] southeast of Well 199-D5-125) and the site of the former 185-D and 190-D buildings (350 m [1,150 ft] southwest of Well 199-D5-125). The 185-D building occupied what is now the 100-D-30 and 100-D-104 waste sites, where Cr(VI) has been detected in near-surface soil. Ongoing remediation will provide additional information on the location of any potential sources of persistent contamination at the 100-D northern plume.

The lower concentrations of Cr(VI) within the northern plume are located near the 116-DR-1&2 Trench, 116-D-7 Retention Basin, and 116-DR-9 Retention Basin. These waste sites received large volumes of cooling water effluent consisting of low concentrations of Cr(VI) and radioactive compounds. The northern Cr(VI) plume extends to the northeast to encompass the area of these three waste sites indicating that they contributed to the Cr(VI) plume (Figure 4-70).

An alternate theory to the northern plume origin is based on historical leakage from the 182-D Reservoir, associated piping, and its location relative to the two plumes. It has been hypothesized that the northern plume has split off from the southern plume and is part of the same source area. The natural flow of groundwater in the aquifer tends to be eastward from 100-D, with groundwater levels at approximately 118 m (387 ft), toward 100-H, where groundwater levels are approximately 116 m (380 ft). However, leaks from the 182-D Reservoir and associated piping, in addition to the artificially enhanced recharge through the

disturbed surface, have caused slight groundwater mounding in some portions of 100-D. The groundwater mound causes a component of the groundwater to flow toward the river, disrupting the natural flow across the Horn. Historical leaks of the 182-D Reservoir may have begun after the plume near the railcar unloading station had begun to migrate to the northeast. As the reservoir began to show signs of wear, leaks from the reservoir and associated piping could have split the plume into two portions. Consequently, both the 100-D southern and the 100-D northern plumes could have originated from the same source.

In addition, the groundwater geochemistry in Well 199-D5-33 shows a good correlation to Columbia River water (Section 3.8). This indicates that although leakage from the reservoir has decreased since water levels were drawn down, the reservoir continues to leak and contribute to the aquifer below. The reduction in leakage has allowed the space between the two plumes at 100-D to lessen. However, clean water introduced from reservoir leakage continues to affect contaminant distribution.

**Seasonal Change.** Changes in the groundwater plume shape and concentration can occur for several reasons. When river stage is high (in the spring), hydraulic head in the river is greater than groundwater hydraulic head. As a result, river water moves inland into bank storage. This causes dilution at the groundwater/surface water interface where clean river water is mixing with Cr(VI) contaminated groundwater, causing Cr(VI) concentrations to be lower in samples collected from monitoring wells and aquifer tubes near the river. As river stage drops, more groundwater discharges to the river from the aquifer(s) causing contaminant levels in nearshore areas to increase. The seasonal variation in Cr(VI) concentrations in groundwater is often greatest adjacent to the river, with less variation and a lag in response time observed farther inland. However, variations in the RUM surface can also affect the distance that seasonal variations may be expected.

Seasonal Cr(VI) concentration trends are most often observed in aquifer tube data. In fall 2009, Cr(VI) concentrations in aquifer tube samples were lower than in spring. Only two (33 percent) of the fall aquifer tube samples had higher Cr(VI) concentrations than the spring samples. In 2011, this trend was even more evident as the fall sample results were below detection (Figure 4-71). This is atypical of most seasonal conditions where the spring freshet will effectively suppress contaminant concentrations in groundwater measured in shoreline aquifer tubes. To further demonstrate the variability in concentrations over time as a result of river stage fluctuations, Figures 4-72 and 4-73 show the plume shape and concentration changes across 100-D in low and high river of 2011. Similar seasonal variation in plume configuration was present in 2012.

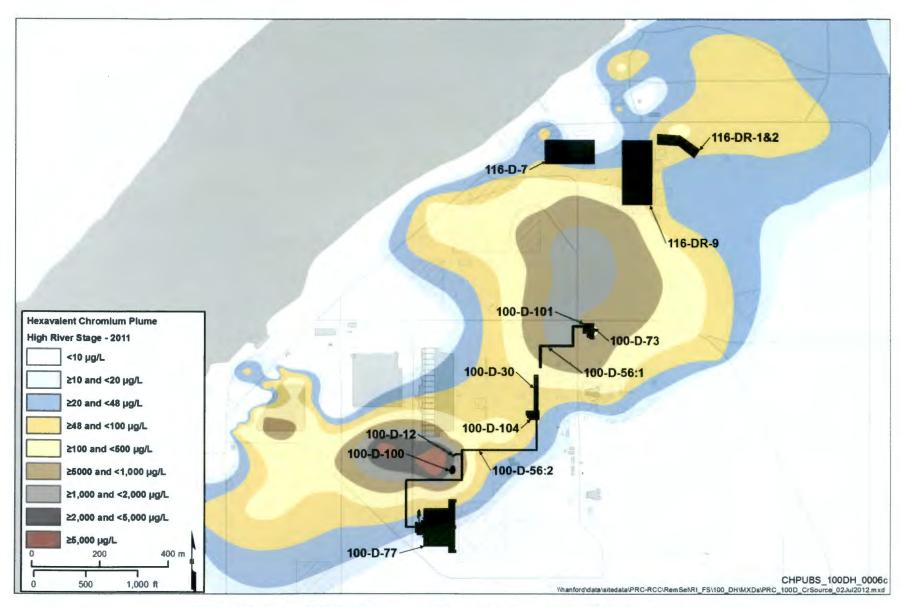


Figure 4-70. 100-D Spring 2011 Cr(VI) Plume and Waste Sites Associated with Sodium Dichromate Use

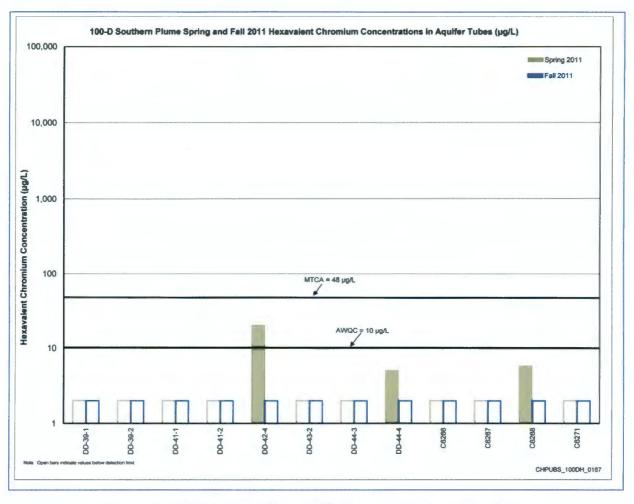


Figure 4-71. 100-D Southern Plume Cr(VI) Concentrations in Aquifer Tubes (Fall and Spring 2011).

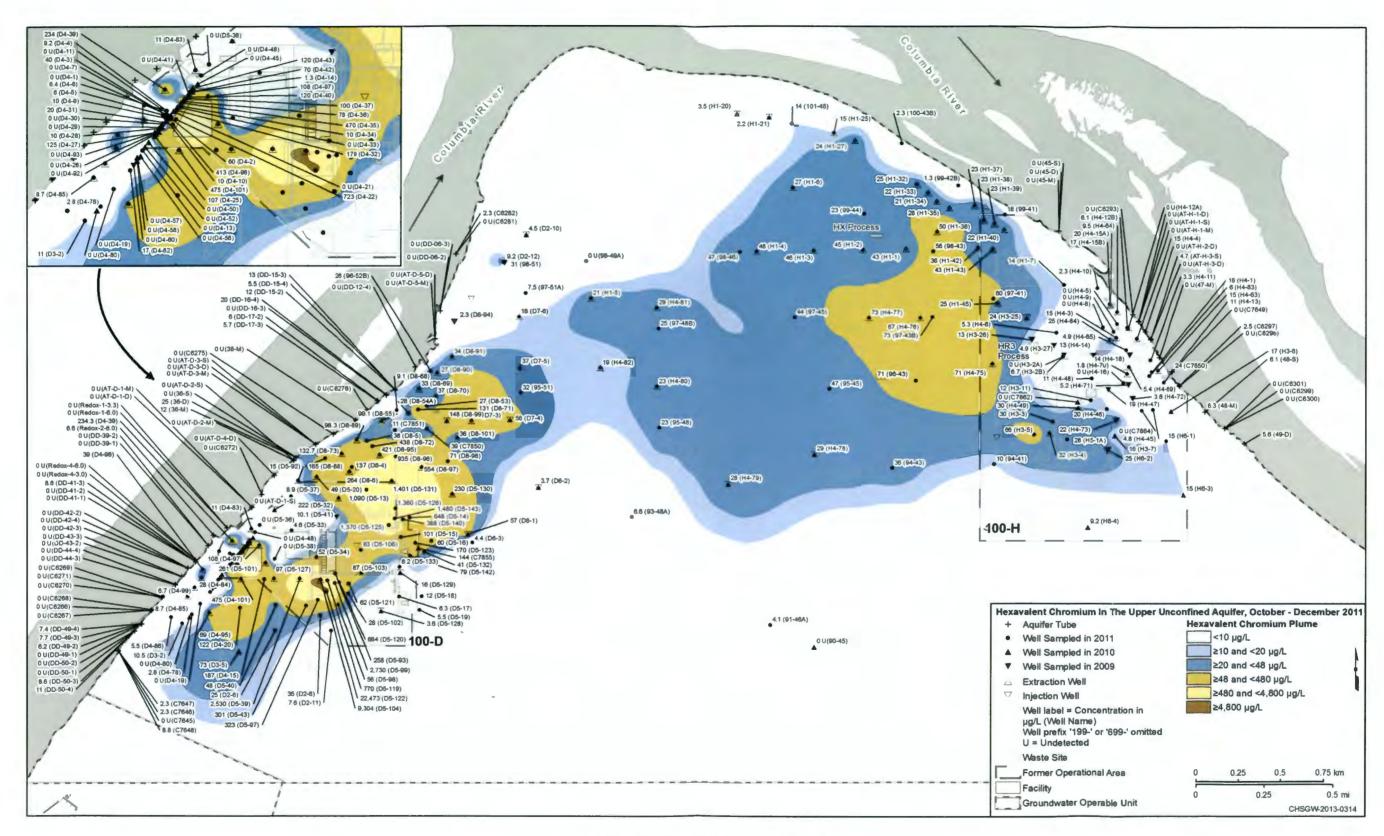


Figure 4-72. Cr(VI) Plume at 100-HR-3 – Low River Stage (2011)

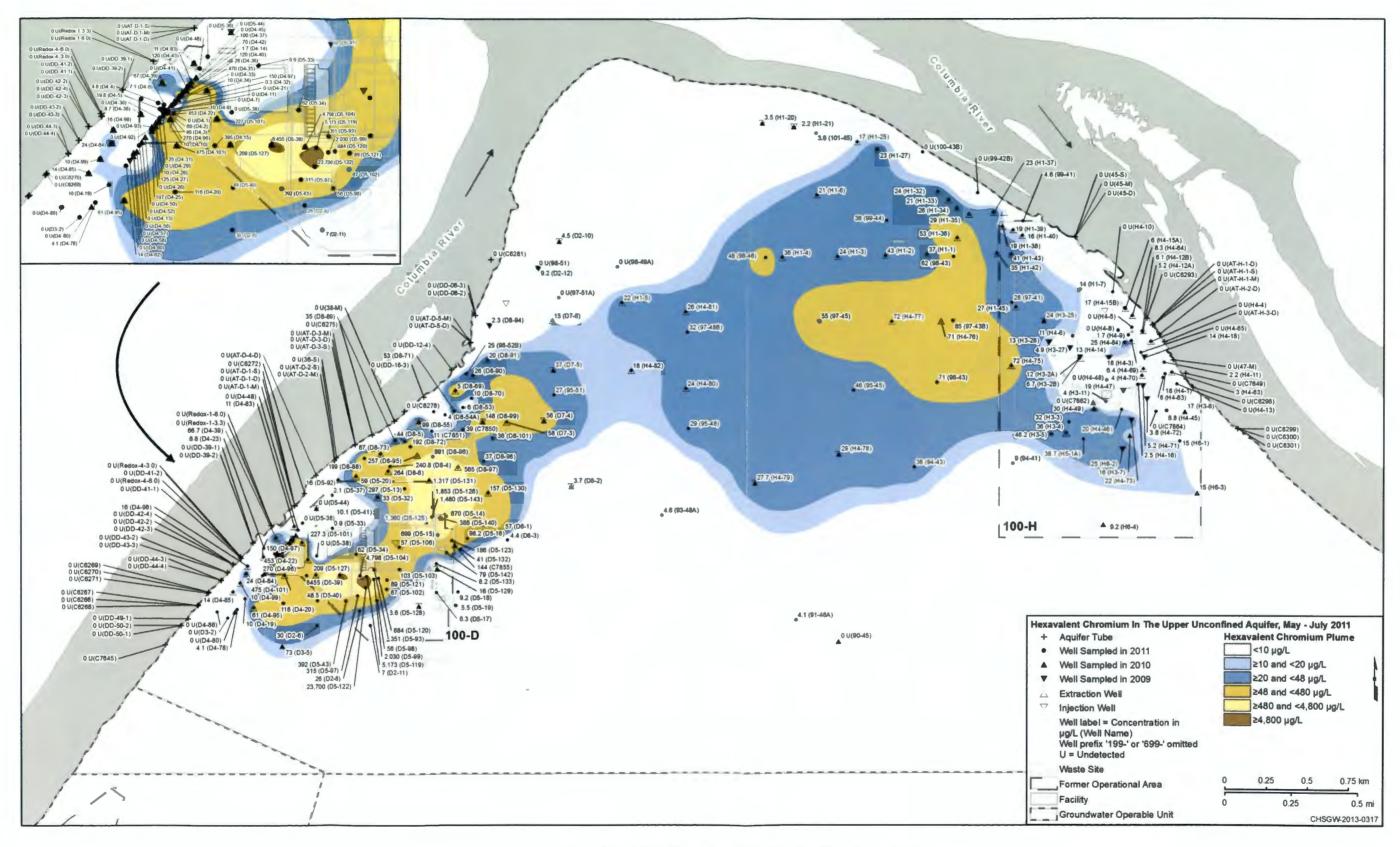


Figure 4-73. Cr(VI) Plume at 100-HR-3 – High River Stage (2011)

Cr(VI) concentrations in northern plume monitoring wells (199-D8-69 and 199-D8-70), which are located on the edge of the plume near the river, have decreased over time (Figure 4-74). A strong seasonal variation was exhibited in these near-river wells, with lowest concentrations often below the state surface water quality standard of 10  $\mu$ g/L in Wells 199-D8-69 and 199-D8-70 during summer sampling rounds. As shown on Figure 4-74, the seasonal fluctuation has been greatly reduced because of the influence of the DX pump-and-treat system, which started operation in December 2010. Seasonal variations are also present in the southern plume wells. However, the seasonal trends are not as dramatic in the southern plume as in Wells 199-D8-69 and 199-D8-70, and so are not presented, and overall concentrations in these wells are decreasing with time.

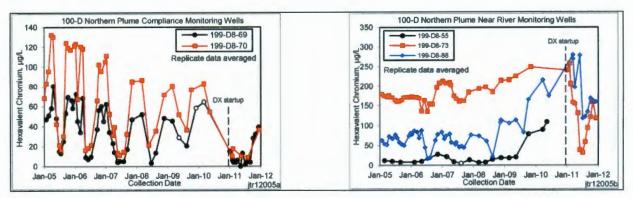


Figure 4-74. Trend Plots for Select Wells in the Northern Cr(VI) Plume at 100-D

The Cr(VI) concentrations in monitoring wells closer to the middle of the northern plume (199-D8-88, 199-D8-55, and 199-D8-73), near the river, were increasing slightly from 2005 through 2010 (Figure 4-74). In 2011, concentrations dropped in response to the DX pump-and-treat system in Wells 199-D8-73 and 199-D8-88. Analytical results from after the startup of the remediation system still show some seasonal fluctuation, but the effects are muted. Well 199-D8-55 has not been monitored since May 2010 and has been converted for use as an injection well for the DX pump-and-treat system.

Remediation Effects. In addition to the influence of the Columbia River, ongoing remediation activities of the vadose zone and unconfined aquifer affect contaminant distribution in the groundwater. Groundwater remediation has been ongoing since 1997 (HR-3 pump-and-treat system) in the northern plume, and since 2004 (DR-5 pump-and-treat system) in the southern plume. As discussed in Section 1.2.3, the older DR system removed substantial Cr(VI) mass but was under designed, pumping only 50 gallons per minute (gal/min). The DX pump-and-treat system, operating at 600 gal/min, began operating in December 2010 and has already affected Cr(VI) concentrations in the southern plume. The areal extent of the Cr(VI) plume in the unconfined aquifer has essentially remained the same to date. However, the DX pump-and-treat system has removed a significant amount of mass from the southern and northern plumes, reducing concentrations in many wells, with the most dramatic effects being exhibited in the higher concentration areas. Cr(VI) concentrations in Well 199-D5-122, located in the southern plume hot spot, decreased significantly from a high of 69,700 μg/L in August 2010 to 9,400 μg/L in September 2011 (Figure 4-75). Concentrations in Well 199-D5-122 continued to decline to 589 μg/L by November 2012, just prior to being decommissioned to allow for continued waste site 100-D-100 remediation.

Groundwater remediation activities in 100-D also included the installation of the ISRM barrier, which was intended to reduce Cr(VI) to a more stable, trivalent form. The ISRM barrier, which intersects the southern end of the Cr(VI) plume, has been largely effective on the south end of the barrier. In response to the ISRM barrier, Cr(VI) concentration trends in groundwater samples from wells both upgradient (199-D5-38, 199-D4-15, 199-D4-20, and 199-D4-22) and downgradient (199-D4-38, 199-D4-23,

199-D4-84, and 199-D4-85) of the barrier are generally decreasing. The barrier was designed to treat levels of Cr(VI) up to 20  $\mu$ g/L using ferric iron. As a result of the higher concentrations encountered at the northern end of the barrier, along with higher groundwater velocities (which resulted in reduced treatment time), some breakthrough was occurring on the northern end of the barrier. As a result, the pump-and-treat system was expanded to capture Cr(VI) that passed through the barrier.

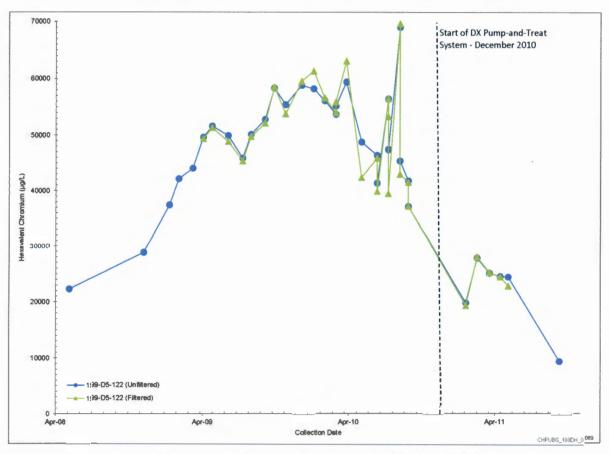


Figure 4-75. Cr(VI) Concentrations over Time: Well 199-D5-122

Ongoing vadose zone remediation at 100-D-100 has removed soil with Cr(VI) present in concentrations up to 774 mg/kg at 10.7 to 13.7 m (35 to 45 ft) bgs and 334 mg/kg at 15.2 m (50 ft) bgs. Remediation of waste sites not only removes contaminated soil, but also reduces the potential for contamination to affect the groundwater (for example, Well 199-D5-122). Groundwater samples from Wells 199-D5-102, 199-D5-98, and 199-D5-99 have all shown a decrease in Cr(VI) concentrations, but the response may be associated with the pump-and-treat operations or with removal of source material. Other well locations have not shown a response to date (Well 199-D5-104), with concentrations remaining stable.

RI Wells in 100-D. Nine groundwater monitoring wells and five boreholes were installed within or adjacent to the 100-D northern and southern Cr(VI) plumes to provide additional data and delineation of the extent of contamination, as part of the RI (Figure 2-1). Of the nine wells, seven were completed in the unconfined aquifer and two were completed in the first water-bearing unit of the RUM. Groundwater samples were collected at discrete depth intervals from open boreholes during drilling. Cr(VI) was detected in groundwater samples during drilling in the unconfined aquifer from each of the RI wells and boreholes at concentrations above  $10~\mu g/L$ . Detections were at various depths within the unconfined aquifer. The result from Well 199-D6-3 was  $17.60~\mu g/L$  at 28.65~m (94 ft) bgs; however, the duplicate sample result was below detection, thus introducing some uncertainty in this result.

Well 199-D3-5 was installed to define the southern extent of the Cr(VI) plume (Figure 2-1) and support data gaps 5 and 13. This well was placed to the south of the 100-D southern hot spot. Contamination was identified at this location, but the well also provides more information on the plume configuration. Cr(VI) concentrations increased with depth in this well, with a result of 73.10  $\mu$ g/L from the sample at the RUM surface, bottom of the unconfined aquifer. This well location correlates with a dip in the RUM surface, which slopes to the south/southwest in that area, away from the 100-D southern plume hot spot (Figure 3-4). As discussed in Section 3.7.1 (Horizontal Hydraulic Gradients and Flow Velocities), groundwater flow direction can shift toward the west (azimuth of 270 degrees) depending on river stage. These two factors indicate that groundwater flow may follow the surface of the RUM in this area. The presence of Cr(VI) at the RUM surface is consistent with such a flow pattern.

During discrete depth sampling, the maximum Cr(VI) concentrations in groundwater ranged from a low of 11  $\mu$ g/L, at a depth of 21 m (69 ft) in borehole C7851, to a high value of 6,520  $\mu$ g/L at a depth of 29.1 m (95.5 ft) in 199-D5-141 (C7625, Well R5). Figure 4-76 shows the maximum Cr(VI) concentrations in groundwater samples collected during drilling, along with the associated sample depth. Vertical distribution data are presented in Section 4.5.3.

Historically, Cr(VI) concentrations in groundwater from the first water-bearing unit in the RUM at 100-D have been consistently below 48  $\mu$ g/L, with sample results below 10  $\mu$ g/L. The single exception is one sample result from Well 199-D8-54B, which had a concentration of 14.6  $\mu$ g/L in May 2008, the maximum concentration for the well. However, the corresponding duplicate sample had a result of 8.3  $\mu$ g/L. With that exception, all other groundwater samples from Well 199-D8-54B have been below 10  $\mu$ g/L. Well 199-D5-134 (C7624, Well R4) and Well 199-D5-141 (C7625, Well R5) were installed as part of this RI/FS effort to confirm the results of the existing well (199-D8-54B).

At Well 199-D5-141, samples collected during drilling indicated Cr(VI) concentrations up to 2,590  $\mu$ g/L in the unconfined aquifer. Cr(VI) was not detected in the first water-bearing unit in the RUM at this location. As there is no contamination present in the underlying aquifer within the RUM at a location where high concentrations are present in the unconfined aquifer, data indicate there is no hydraulic connection between the two water-bearing units at the well. Well 199-D5-141 was screened across the water-bearing unit in the RUM and samples from the completed well represent that aquifer. Monitoring Well 199-D5-144 (C8668, Well R5 redrill) was located closer to the 100-D-12 waste site (and upgradient from Well 199-D5-141); however, Cr(VI) values in the unconfined aquifer were lower than those detected in groundwater from Well 199-D5-141.

In Well 199-D5-134 (C7624, Well R4), samples collected during drilling indicated Cr(VI) concentrations up to 1,670  $\mu$ g/L in the unconfined aquifer. Also from samples collected during drilling, both total chromium and Cr(VI) were detected in the first water-bearing unit of the RUM. Total chromium concentrations were at 12.6  $\mu$ g/L and Cr(VI) concentrations were at 12.2  $\mu$ g/L. An evaluation of the boring logs and daily reports indicates that the sample was collected following difficulty in sample collection, which resulted in a delay of more than 2 days. Based on an evaluation of the sample results at this well, presented with the vertical distribution discussion, it is likely that this sample was contaminated from groundwater originating from the unconfined aquifer, and is not representative of the first water-bearing unit in the RUM. A post-installation sample from January 2012 had a concentration below detection, confirming that contamination is not present in the confined aquifer.

During drilling activities, groundwater samples were collected from the second water-bearing unit in the RUM, presumed to be the Ringold Formation unit B, in Wells 199-D5-141 and 199-D5-134 to evaluate the presence of contaminants in the lower aquifer. Total chromium and Cr(VI) concentrations in these samples were below the laboratory detection limits. Vertical distribution data are presented in Section 4.5.2.

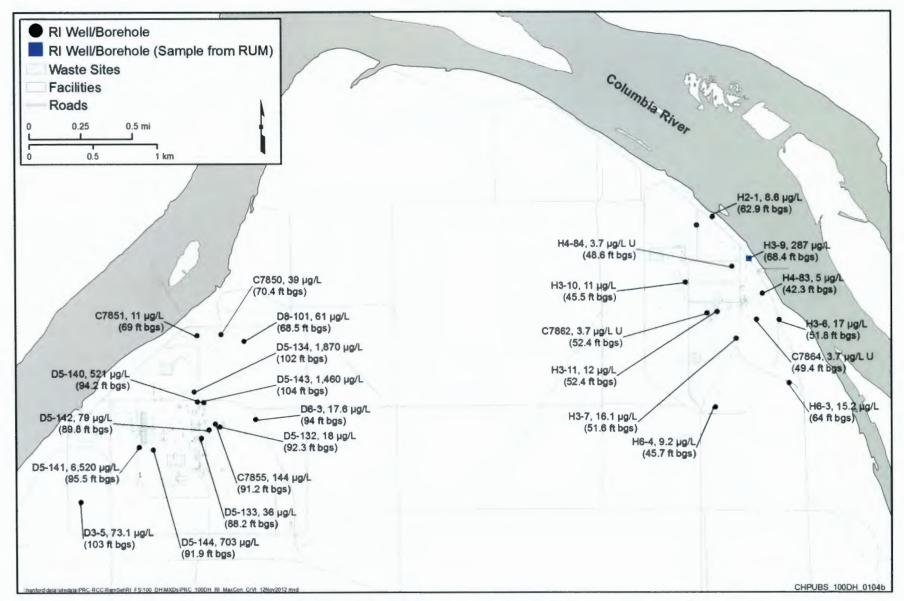


Figure 4-76. Maximum Cr(VI) Concentrations in Borehole Water Samples from RI Wells

### 4.5.1.2 Horn Area

Groundwater in the Horn generally exhibits much lower Cr(VI) concentrations than those found in the 100-D plumes, although concentrations still exceed the state surface water quality standard of 10  $\mu$ g/L and the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) level of 48  $\mu$ g/L at many locations. Figure 4-77 shows the Cr(VI) concentrations for wells completed in the RUM, including those in the Horn. The Horn has very few waste sites; therefore, the Cr(VI) detected in the groundwater likely migrated across the Horn from 100-D rather than having originated from local releases. Other waste sites in the area, such as 600-105, are located to the south with Cr(VI) levels below 5  $\mu$ g/L, and are unlikely contributors to the main Cr(VI) plume.

Concentration trends in the Horn groundwater monitoring wells are generally decreasing or stable. The maximum Cr(VI) detection was 117  $\mu$ g/L in Well 699-97-43B (October 2007). Cr(VI) concentrations in aquifer tube samples located along the eastern side of the Horn (44-D, C5634, C5637, C5641, and C5674) are also generally stable or decreasing.

Three wells in the Horn are completed in the RUM: Wells 699-97-43C, 699-97-45B, and 699-97-48C. Cr(VI) concentrations have been consistently below the laboratory detection limits from Wells 699-97-43C and 699-97-45B, the area closest to 100-H. Groundwater samples from Well 699-97-48C (Figure 4-78), located downgradient from the 116-DR-1&2 Trench, have shown an overall increasing Cr(VI) concentration trend, with concentrations up to  $62.6~\mu g/L$  in November 2012.

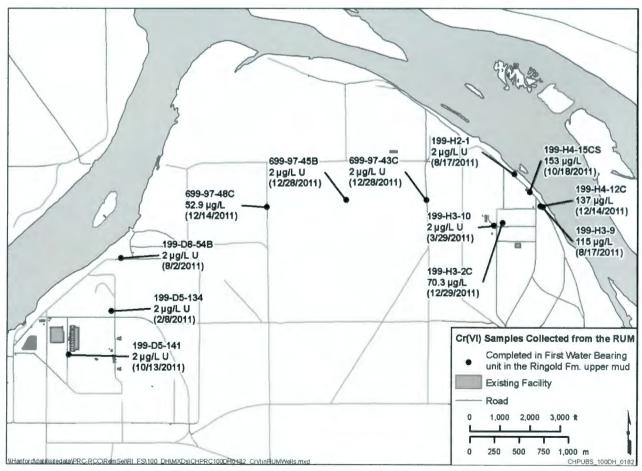


Figure 4-77. Monitoring Wells Completed in the RUM

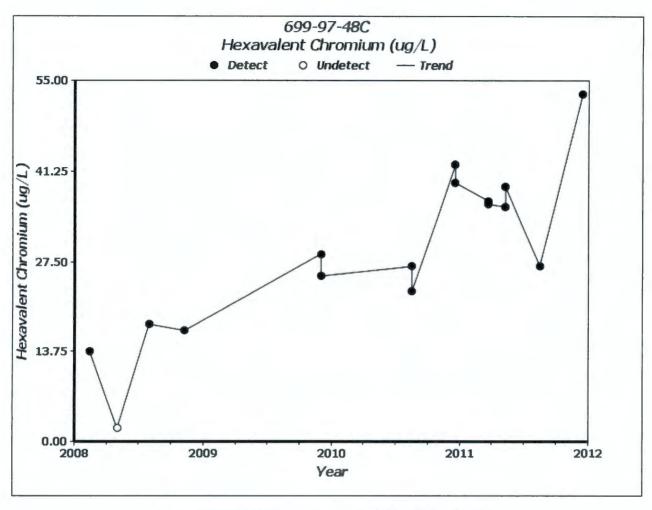


Figure 4-78. Cr(VI) Concentrations in RUM Well 699-97-48C

**Seasonal Changes.** Aquifer tubes in the Horn were not sampled for Cr(VI) in fall 2009 or spring 2010. In groundwater monitoring wells, the Cr(VI) concentrations greater than 10  $\mu$ g/L were measured in nine (82 percent) of the fall 2009 and spring 2010 groundwater samples (Figure 4-79). The seasonal variation in groundwater monitoring wells across the Horn is not consistent in the area.

Overall, the Cr(VI) concentrations across the Horn near 100-D are below 48  $\mu$ g/L, with concentrations generally showing a decreasing trend in the unconfined aquifer. Because the mass of Cr(VI) continues to migrate to the east with the groundwater flow, Cr(VI) concentrations increase on the eastern side of the Horn with concentrations as high as 85  $\mu$ g/L at Well 699-97-43B. The HX pump-and-treat system extraction and injection wells have largely remediated the area at 100-H and have formed a barrier to further migration of Cr(VI) from the Horn towards the river.

No monitoring wells were drilled in the Horn as part of the RI. However, 25 RPO wells were installed in the Horn from 2009 to 2010. The additional sampling, together with previous monitoring, indicates that the Cr(VI) plume underlying the Horn has remained relatively stable, and is slowly migrating toward 100-H. There continues to be an area of groundwater with concentrations slightly greater than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) level of 48  $\mu$ g/L near 100-H.

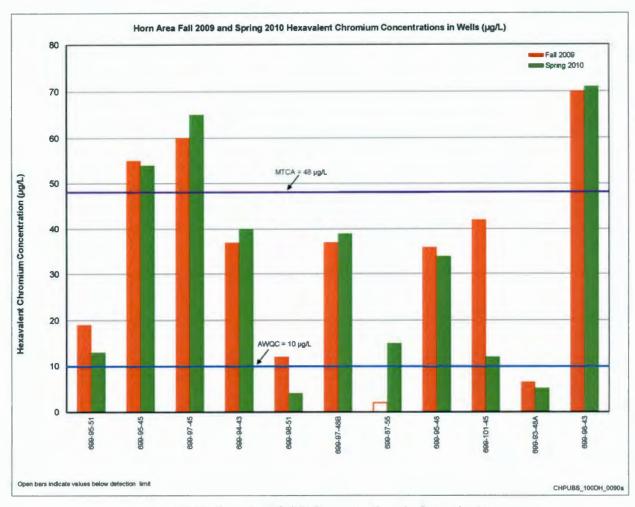


Figure 4-79. Horn Area Cr(VI) Concentrations in Groundwater from Wells – Fall 2009 and Spring 2010

### 4.5.1.3 100-H Area

The Cr(VI) plume at 100-H (Figure 4-80) is characterized by much lower concentrations than the 100-D plumes (Figures 4-70 and 4-71). Cr(VI) concentrations in the unconfined aquifer are not detected above 100  $\mu$ g/L in 100-H; however, samples from most areas of 100-H exceed the state surface water quality standard of 10  $\mu$ g/L. The maximum concentration in the unconfined aquifer was 91.8  $\mu$ g/L in Well 199-H1-43 (March 2010). Monitoring wells installed as part of the RI, and completed in the first water bearing unit of the RUM had concentrations as high as 287  $\mu$ g/L (Well 199-H3-9).

Facilities and waste sites associated with former sodium dichromate handling are potential sources of Cr(VI) contamination. In 100-H, these include the following facilities and waste sites: 116-H-1 Trench, 116-H-2 Trench and associated overflow (100-H-17 waste site), 116-H-4 Pluto Crib, 183-H Solar Evaporation Basins (116-H-6 waste site), 116-H-7 Retention Basin, and 105-H Reactor Fuel Storage Basin. Other potential or suspected sources of Cr(VI) include the 190-H sodium dichromate handling facilities (100-H-46 waste site), 100-H-21 effluent pipelines, and 100-H-5 sludge trench. The relationship of these waste sites to the current Cr(VI) plume is shown on Figure 4-80. The groundwater mound at 100-H was not as extensive as at 100-D, but originated primarily from the 116-H-7 Retention Basin and leaked at rates as high as 38,000 L/min (10,000 gpm).

100-D is an additional source of Cr(VI) in the unconfined aquifer at 100-H, primarily because of the 1967 infiltration test, when cooling water discharges to the 116-H-7 were redirected to the 116-DR-1 & 2 Trench. As discussed in Chapter 1 (Section 1.2.3), the infiltration test resulted in approximately  $1.3 \times 10^{10}$  L ( $3.4 \times 10^{9}$  gal) of cooling water effluent being discharged to the 116-DR-1&2 Trench (*Program Review—Ground Disposal of Reactor Effluent* [DUN-3259]). The effluent caused an additional 2.7 to 3 m (9 to 10 ft) of groundwater mounding beyond that caused by ongoing operations, with Cr(VI) concentrations estimated at 350  $\mu$ g/L. The subsequent groundwater mound migrated eastward, affecting the unconfined aquifer in the Horn and 100-H.

Unlike 100-D, contamination has been detected in the first water-bearing unit of the RUM at 100-H. As discussed in Chapter 3, the geologic conditions at 100-H are different from those at 100-D. The key stratigraphy at 100-H, as compared to 100-D, includes the following features:

- Thinner vadose zone and unconfined aquifer
- Ringold Formation unit E is not present
- Variation in RUM material between the unconfined aquifer and the first water-bearing unit

At 100-D, the RUM is typically identified at about 27 to 35 m (90 to 115 ft) bgs. This same unit is identified at 100-H at about 10 to 18 m (35 to 60 ft) bgs, with some variability in both areas. The first portion of the RUM is therefore about 17 m (55 ft) thinner at 100-H, making it more vulnerable to hydraulic head changes in the overlying aquifer. More importantly, the first portion of the RUM appears to have a greater sand and gravel component at 100-H than the same zone at 100-D, contributing to the vulnerability of the first water bearing unit in the RUM.

These stratigraphic features, combined with high head conditions created from the groundwater mound at the 116-H-7 Retention Basin during reactor operations, are the likely reasons for contamination in the RUM at 100-H and not in 100-D. The pressure of the mound at 100-H could have pushed the contaminated groundwater into the first of the lower aquifers. Section 4.5.3 discusses the vertical distribution of Cr(VI), and includes the analytical sample results from the deeper units.

Seasonal Change. Figures 4-70 and 4-71 show the seasonal variation of Cr(VI) plume configuration at 100-D/H. As in 100-D, seasonal variability at 100-H is observed mainly adjacent to the river, with minimal seasonal variation inland. Figure 4-81 shows Cr(VI) fall 2009 and spring 2010 concentrations for 100-H wells. 100-H aquifer tubes were not sampled for Cr(VI) in fall 2009 or spring 2010. Cr(VI) concentrations greater than the state surface water quality standard of 10  $\mu$ g/L were measured in 10 (48 percent) of the fall 2009 groundwater samples and 13 (62 percent) of the spring 2010 samples. Concentrations greater than the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) level of 48  $\mu$ g/L were measured in three (14 percent) of the fall 2009 groundwater samples and four (19 percent) of the spring 2010 groundwater samples. In contrast to other 100-D/H areas described previously, fall 2009 concentrations were lower than spring 2010 concentrations. The fall 2009 concentrations were greater than spring 2010 concentrations in only eight (38 percent) of the monitoring wells. This pattern is more typical of the seasonal variations along the Columbia River, and was identified at 100-H during the 2009 to 2010 time frame, resulting in part from the different lithology of the aquifer matrix.

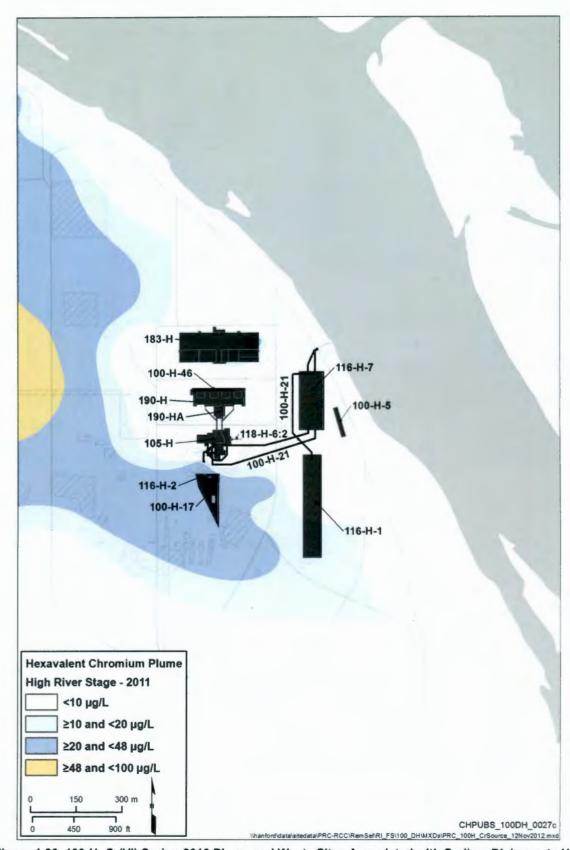


Figure 4-80. 100-H: Cr(VI) Spring 2010 Plume and Waste Sites Associated with Sodium Dichromate Use

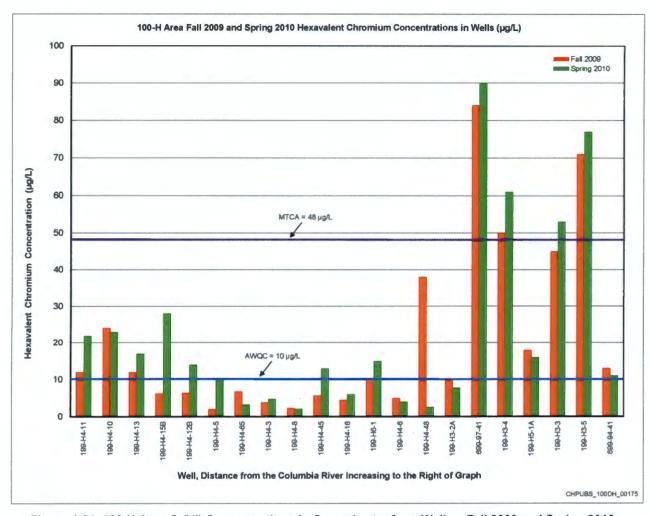


Figure 4-81. 100-H Area Cr(VI) Concentrations in Groundwater from Wells - Fall 2009 and Spring 2010

Remediation Effects. Unlike the Cr(VI) plumes in 100-D, the 100-H plume has diminished substantially in recent years, as evidenced by decreasing Cr(VI) concentrations in the unconfined aquifer extraction wells (199-H4-3, 199-H4-63, and 199-H4-15A). This result is directly caused by the operation of the interim remedy HR-3 pump-and-treat system. On October 1, 2011, the HX pump-and-treat system was started with a capacity of 3,000 L/min (800 gal/min). This new system is expected to facilitate remediation because of the expanded capture area. The remediation system is aided by the hydrogeology of the area, which includes an aquifer matrix (that is, Hanford formation) with more favorable hydraulic properties than at 100-D, and a relatively thin unconfined aquifer. The Cr(VI) concentrations in the majority of unconfined aquifer wells at 100-H show a decreasing trend. Figure 4-82 shows representative trends from wells in the northern, northwestern, and southeastern portions of 100-H (Wells 199-H4-15B, 199-H4-8, and 199-H4-45, respectively).

Monitoring wells in the southwestern portion of 100-H do not follow the same trend, exhibiting either stable or increasing Cr(VI) concentrations. This suggests continued migration of Cr(VI) with groundwater flow in the unconfined aquifer from the Horn to the southeast.

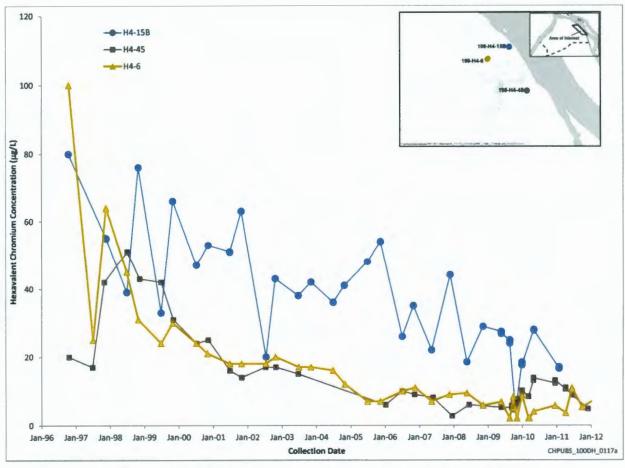


Figure 4-82. Cr(VI) Trends in Groundwater for Select Wells in 100-H

Cr(VI) in the RUM. The RUM is generally considered an aquitard, which means it cannot transmit significant amounts of water, but may store water. Aquitards, which are often considered leaky confining beds, can transmit small amounts of water between stratigraphic units. Along the river corridor, the uneven RUM surface forms the base of the unconfined aquifer, and contains several water-bearing sandy gravel lenses. At 100-H, the material present between the RUM surface and the first water-bearing unit is typically described as sandy silt or gravelly silt. This can be compared to the same zone at 100-D, which is generally described as silt and silty clay material with lenses of "thick" or "hardened" clay. In addition, based on the existing RUM wells, the material in this zone is nearly 17 m (55 ft) thicker at 100-D than in most areas of 100-H, with some variability between wells. In areas such as at 100-H, where the first water-bearing unit in the RUM is closer to the RUM surface, and the RUM material itself is more permeable and may allow water to be transmitted between stratigraphic units, a hydraulic connection between the unconfined aquifer and the water-bearing units within the RUM may be present.

Under certain conditions, this connection may transmit contamination in addition to water. One such condition may be the discharge of large volumes of cooling water that occurred near the former 105-H Reactor, which caused a mound of groundwater to form 4.9 to 10.1 m (16 to 33 ft) above the natural water table. At 100-H, the groundwater mound was primarily associated with the 116-H-7 and 116-H-1 Retention Basins, which is located just south of the highest levels of Cr(VI) contamination within the first water bearing unit of the RUM. The high head conditions associated with the groundwater mound during operations may have driven groundwater contaminated with Cr(VI), consistent with cooling water, into the first water-bearing unit in the RUM via a hydraulic connection between this unit and the unconfined

aquifer (Section 3.7.3 and Section 3.7.4). This is supported by the observed higher concentrations of Cr(VI) in the RUM as compared to the overlying unconfined aquifer (Figure 4-83), with the RI well data presented in Figure 4-84. Figure 4-83 presents a plume map of the contamination identified in the RUM at 100-H based on the historic maximum concentrations, and using a quantile kriging methodology. Another condition that supports a connection between the retention basins and the presence of Cr(VI) in the RUM along the Columbia River shoreline is the undulating surface of the RUM itself. The zones of contamination within the permeable units of the RUM coincide with low spots in the RUM surface. This indicates an area where the RUM surface is scoured, and therefore thinner, which results in a location where increased hydraulic pressures from above may create a potential pathway for contaminants.

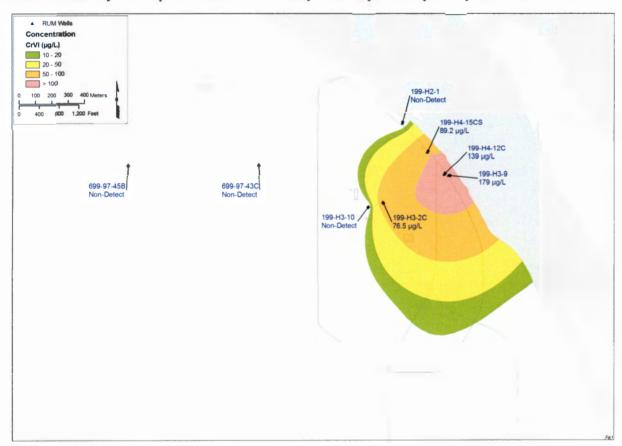


Figure 4-83. Extent of Cr(VI) Contamination within the RUM at 100-H

In 2009, an aquifer test and rebound study was conducted at 100-H (*Aquifer Testing and Rebound Study in Support of the 100-H Deep Chromium Investigation* [SGW-47776]). Testing was conducted at three 100-H wells/piezometers that were completed in the first water-bearing unit of the RUM (Wells 199-H3-2C, 199-H4-12C, and 199-H4-15CS). All three of these wells showed a marked response to the aquifer tests conducted from August 20 to November 11, 2009. During that time, step-drawdown pump tests and subsequent constant rate pump tests were conducted at all three of the wells. Details on the aquifer characteristics of these wells and their interactions are discussed in Section 3.7.2, Section 3.7.3, and Section 3.7.4. The wells closest to the Columbia River had Cr(VI) concentrations above 20  $\mu$ g/L prior to the pumping and rebound tests, with the Cr(VI) concentrations at inland Well 199-H3-2C slightly below 20  $\mu$ g/L. After pumping was suspended, Cr(VI) concentrations in these three wells continued to show a gradually increasing trend, reaching 148  $\mu$ g/L in Well 199-H4-12C by March 2011 and 153  $\mu$ g/L in piezometer 199-H4-15CS.

Three additional wells were completed in the RUM at 100-H as part of this RI: Wells 199-H2-1, 199-H3-9, and 199-H3-10. Figure 4-84 shows Cr(VI) concentration trends from the wells currently completed within the RUM, with results from the last sampling event from 2011 posted. As discussed in Section 4.4.2, Cr(VI) was detected at 8.6  $\mu$ g/L in the first water-bearing unit of the RUM in Well 199-H2-1 during drilling. Post-installation samples from Well 199-H2-1 were below detection. Cr(VI) concentrations at Well 199-H3-9 were as high as 287  $\mu$ g/L during drilling. Cr(VI) was not detected in the first water-bearing unit of the RUM at Well 199-H3-10.

A comparison of groundwater levels in 199-H4-15 nested piezometers suggests that an upward hydraulic gradient exists between the unconfined aquifer and lower water-bearing units below the RUM (Chapter 3, Section 3.7.2.2). This relationship would tend to retard migration of contaminants from the upper units except under unique circumstances, such as the presence of high hydraulic head. However, the steepness of the upward vertical gradient has decreased in recent years. This decrease in vertical gradient may help explain concentration trends in both the semiconfined and the confined water-bearing units in the Ringold Formation. Piezometer 199-H4-15CS is completed in the first water-bearing unit in the RUM, and 199-H4-15CQ is completed in the second water-bearing unit, presumed to be Ringold unit B. Piezometer 199-H4-15CR is completed in the RLM, and 199-H4-15CP is completed in the basalt unit. The Cr(VI) concentrations for the 100-H deep piezometer cluster 199-H4-15CP, 199-H4-15CQ, and 199-H4-15CR are all below the state surface water quality standard value of 10 μg/L.

RI Wells. Eight RI groundwater monitoring wells and five boreholes were installed in or adjacent to the 100-H plume to provide additional data and to further delineate the extent of contamination. Five of the monitoring wells were drilled into the top of the RUM to an average depth of 19.2 m (62.9 ft) bgs and screened in the unconfined aquifer. Groundwater samples were collected from boreholes during drilling at depth discrete intervals. The Cr(VI) concentrations in groundwater samples from the unconfined aquifer (boreholes and wells) ranged from nondetect in a few locations to 25 μg/L at a depth of 14.3 m (47.0 ft) in Well 199-H4-84. Sample results for the remaining locations were between 3.7 and 16.1 μg/L.

Three monitoring wells were drilled into the first water-bearing unit in the RUM to an average depth of 64.8 m (212.6 ft). Within the first water-bearing unit of the RUM, the Cr(VI) concentrations ranged from below detection to a maximum value of 287  $\mu$ g/L at a depth of 20.8 m (68.4 ft) in Well 199-H3-9 (C7639, Well R1). Figure 4-84 shows Cr(VI) maximum concentrations and associated depths in all new RI wells.

During drilling activities, groundwater samples were collected from Wells 199-H2-1, 199-H3-9, and 199-H3-10 to evaluate the presence of contamination, including total chromium and Cr(VI) in some of the deeper water-bearing units within the RUM, with the first of these presumed to be unit B. Total chromium and Cr(VI) concentrations in these groundwater samples were below the laboratory detection limits. Vertical distribution data are presented later in this section.

# 4.5.1.4 Hexavalent Chromium in Aquifer Tubes

Additional Cr(VI) aquifer tube data from the 2011 annual report (*Hanford Site Groundwater Monitoring for 2011* [DOE/RL-2011-118]) are presented on Figures 4-85 through 4-93 and discussed in the following paragraphs.

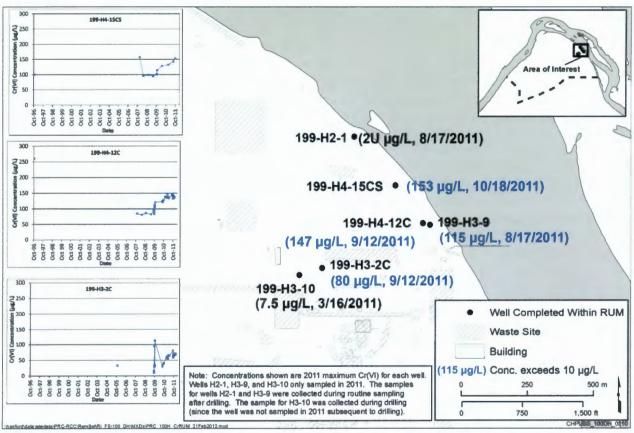


Figure 4-84. Cr(VI) Distribution in the First Water-Bearing Unit in the RUM -RI Wells

Figure 4-85 shows the historical range and the maximum Cr(VI) concentrations in 100–D aquifer tubes. At most sites, the 2011 concentrations were at the lower end of the historical range. Figure 4-86 shows fall 2011 Cr(VI) concentrations with depth in a cross–section near the ISRM barrier and southern Cr(VI) plume from upstream to downstream aquifer tubes at 100-D. The Cr(VI) concentrations in 2011 were the highest in aquifer tube DD-50 at 10.6  $\mu g/L$ ; however some locations were not sampled during 2011. Cr(VI) concentrations in aquifer tubes downgradient of the northern plume have generally declined since the late 1990s (Figure 4-87), although exhibiting some seasonal variation. Figure 4-87 shows results for aquifer tubes near the northern Cr(VI) plume. Throughout 100-D, Cr(VI) concentrations are significantly lower in 2011 than in previous years, with analytical results below 25  $\mu g/L$  at all sampled locations except Redox-1-6.0. Concentrations in Redox-1-6.0 were at 96.70  $\mu g/L$  in January 2011, but decreased to below detection by fall of 2011. The Cr(VI) concentrations in aquifer tube Redox-1-6, which had a value of 384  $\mu g/L$  in 2009.

Figure 4-88 shows the historical range and the maximum Cr(VI) concentrations in 100–H aquifer tubes. Figures 4-89 and 4-90 show the fall 2011 Cr(VI) concentrations with depth in a cross-section through aquifer tubes from the east side of the Horn area and through 100-H. Cr(VI) concentrations in aquifer tubes in the main 100-H area were below 10  $\mu g/L$  with the exception of aquifer tube C7650, which had a concentration of 26.6  $\mu g/L$  in December 2011. Concentrations along the Horn area were all less than the state surface water quality standard value of 10  $\mu g/L$ , excluding C6287.

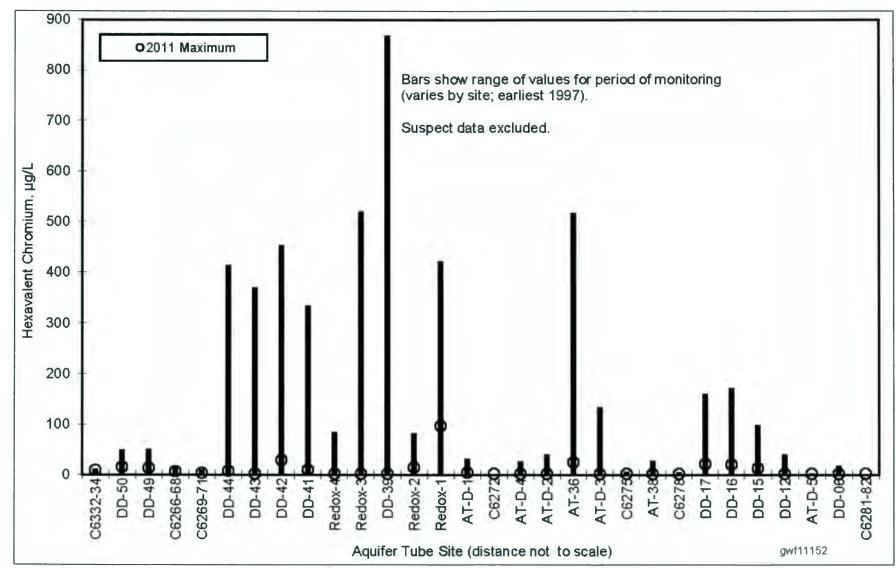


Figure 4-85. 100-D Area Aquifer Tubes – Historical Data Range

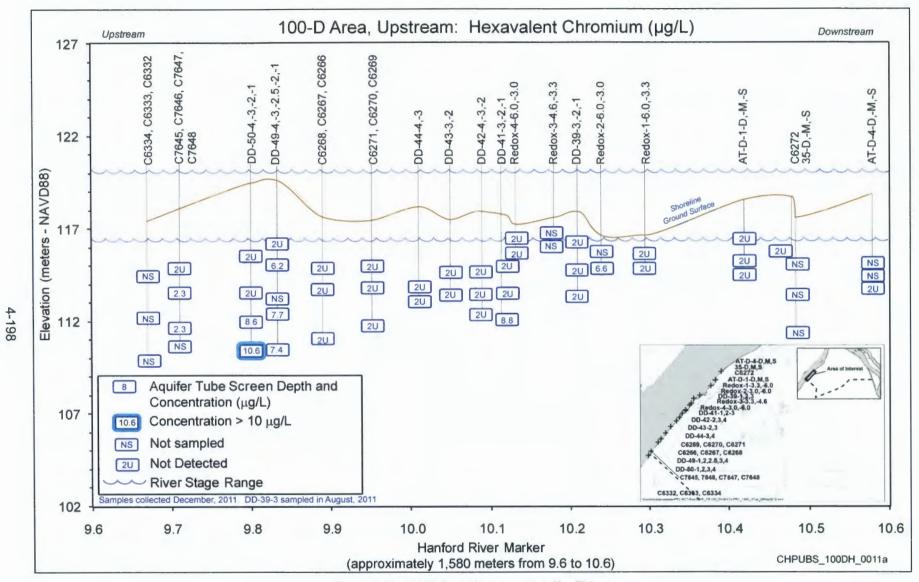
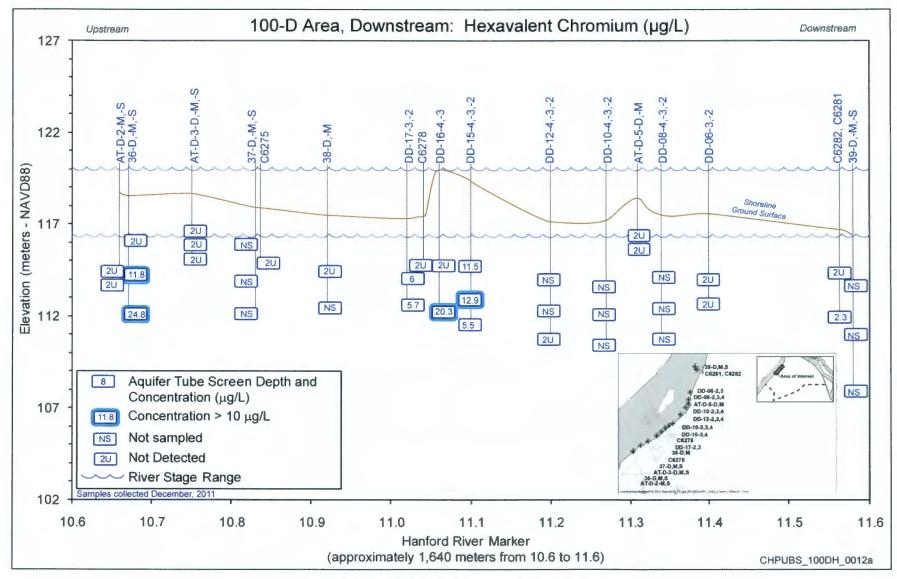


Figure 4-86. 100-D Area Upstream Aquifer Tubes



4-199

Figure 4-87. 100-D Area Downstream Aquifer Tubes

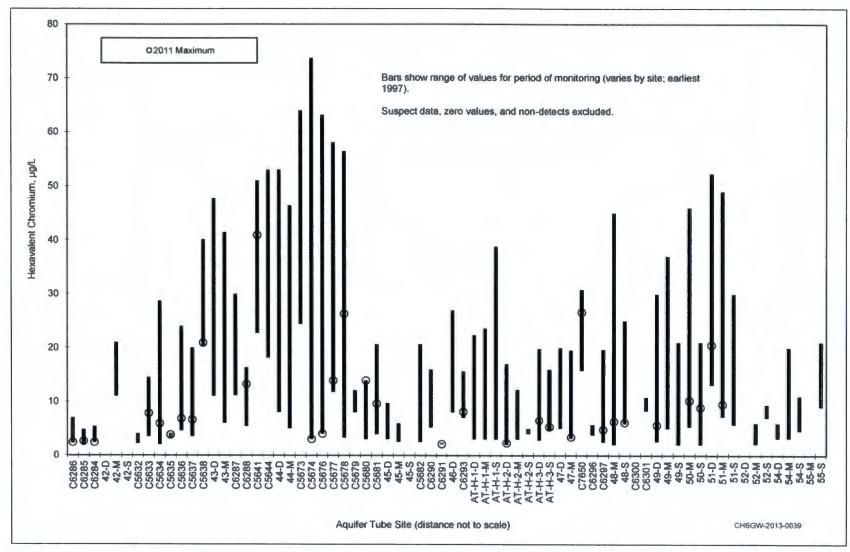


Figure 4-88. 100-H Area Aquifer Tubes – Historical Data Range

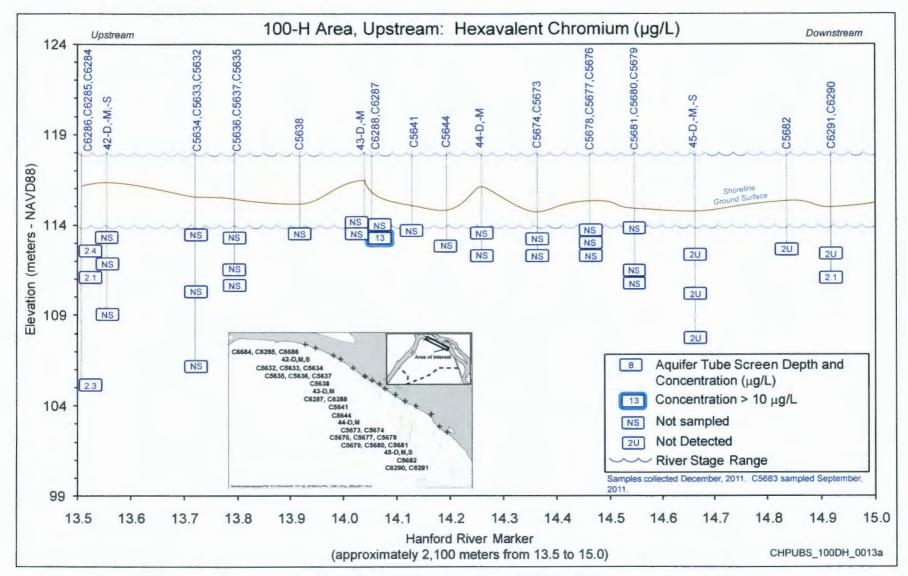


Figure 4-89. 100-H Area Upstream Aquifer Tubes

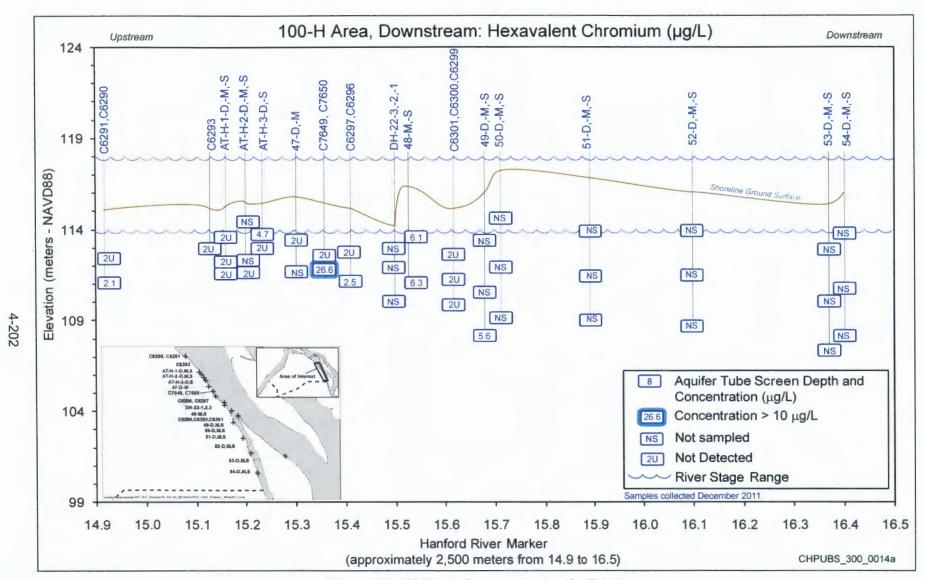


Figure 4-90. 100-H Area Downstream Aquifer Tubes

Six new aquifer tubes were installed to meet the criteria of data need 5 (100-D/H Work Plan [DOE/RL-2008-46-ADD1]). The four new aquifer tubes at 100-D (C7645, C7646, C7647, C7648) were installed to define the lateral extent of contamination southwest of the ISRM barrier, while the two new aquifer tubes at 100-H (C7649 and C7650) were installed to define the extent of contamination between the 116-H-7 Retention Basins and the river. Data collected from the four 100-D aquifer tubes indicated that Cr(VI) concentrations are less than 10  $\mu$ g/L. At 100-H, aquifer tube C7649 had Cr(VI) concentrations below detection limits. Aquifer tube C7650 had 26.6  $\mu$ g/L of Cr(VI) detected in fall 2011, with 2010 results ranging from 6.6  $\mu$ g/L in August to 30.8  $\mu$ g/L in December. Aquifer tube data from 100-D/H generally indicate that Cr(VI) concentrations are less than the state surface water quality standard of 10  $\mu$ g/L, with few exceptions.

Overall, concentrations in aquifer tubes decreased during 2012, with the higher concentrations found in locations consistent with previous years. The highest concentration of Cr(VI) found in aquifer tubes of 100-D/H during 2012 was 33.9  $\mu$ g/L in aquifer tube C5641, located in 100-H. The highest concentrations in 100-D during 2012 was 24.7 in aquifer tube DD-41 located near the northern end of the ISRM barrier.

## 4.5.2 Vertical Distribution of Hexavalent Chromium

The distribution of contaminants is important to understand not just horizontally, but also vertically, to ensure that the plume is well defined. For example, a well that is completed in the top of an aquifer may not indicate the presence of an analyte that is denser than water, and is therefore only present at the bottom of that unit or in a deeper water-bearing zone. To evaluate the vertical distribution of Cr(VI), existing wells were sampled at discrete depths, and wells installed during the RI were sampled at discrete depths during drilling.

Four existing wells were sampled in early 2011 using rigid porous polyethylene (RPP) samplers: Well 199-D5-99, 199-D5-122, 199-D5-126, 199-D, and 699-97-45. Each well was equipped with four RPP passive samplers placed at different depth intervals within each well to evaluate the vertical stratification of Cr(VI) within the unconfined aquifer. Groundwater monitoring Well 199-D5-99 is located near the former 100-D-12 French Drain waste site, in the southern 100-D plume, Well 199-D5-122 is located in the hot spot of the southern 100-D plume, and Well 199-D5-126 is located within the hot spot of the northern 100-D plume. Monitoring Well 699-97-45 is located in the Horn, and unlike the other wells is screened in the Hanford formation.

Predetermined depth intervals of each RPP sampler were based on where the water table and RUM surface were encountered at each well location. RPP sampler placement was as follows: at the water table, straddling the screen at the RUM surface, at 0.6 to 0.9 m (2 to 3 ft) above the RUM surface, and between the upper and intermediate RPP. The results of the study are reported in *Cr(VI) Density Stratification Study*, 100-D Area, Hanford Site, Washington (SGW-49739).

As shown in Table 4-20, the Cr(VI) results from Wells 199-D5-99 and 199-D5-122 indicate the presence of some vertical stratification in the unconfined aquifer with higher concentrations near the bottom of the aquifer. The RPP sampling conducted in Well 199-D5-99 showed the greatest vertical Cr(VI) stratification at 100-D, because concentrations in the upper 75 percent of the unconfined aquifer were at approximately 1,500  $\mu$ g/L, then increased 9,960  $\mu$ g/L in the RPP sampler placed at the RUM surface. This well is located near waste site 100-D-100 and the former railcar unloading facility.

Concentrations in Well 199-D5-122 were higher in the lower 75 percent of the unconfined aquifer, with concentrations of about 26,000  $\mu$ g/L. The RPP sample from the top of the aquifer had Cr(VI) at 6,590  $\mu$ g/L. However, as with Well 199-D5-99, the variation is found in a single well and lacks an apparent downward or increasing trend. This is more indicative of variation within the water column than actual stratification trends.

Table 4-20. Vertical Distribution of Cr(VI) in Four 100-D/H Unconfined Aquifer Wells

Well Name (Borehole ID)	General Location	Sample Depth m (ft) bgs	Date Collected	Sample ID (HEIS #)	Cr(VI) Sample Results (μg/L)
199-D5-99	100-D,	26.46 (86.80)	1/17/2011	B2BDM5	1,440
(C5392)	Southern	28.80 (94.50)	1/17/2011	B2BDM6	1,460
	Plume	32.46 (106.50)	1/17/2011	B2BDM7	1,490
		33.38 (109.50)	1/17/2011	B2BDM8	9,960
199-D5-122	100-D,	26.44 (86.75)	1/17/2011	B2BDN0	6,590
(C5936)	Southern	28.96 (95.00)	.46 (106.50)       1/17/2011       B2BDM7         .38 (109.50)       1/17/2011       B2BDM8         .44 (86.75)       1/17/2011       B2BDN0         3.96 (95.00)       1/17/2011       B2BDN1         .85 (104.50)       1/17/2011       B2BDN2         .77 (107.50)       1/17/2011       B2BDN3         3.42 (86.68)       1/31/2011       B2BDN5         3.73 (94.25)       1/31/2011       B2BDN6         .54 (106.75)       1/31/2011       B2BDN7	25,700	
	Plume	31.85 (104.50)	1/17/2011	B2BDN2	26,200
		32.77 (107.50)	1/17/2011	B2BDN3	26,900
199-D5-126	5-126 100-D, 26.42 (86.68) 1/31/2011 B2BDN5	1,510			
(C6390)		28.73 (94.25)	1/31/2011	B2BDN6	1,510
	Plume	32.54 (106.75)	1/31/2011	B2BDN7	1,520
		33.45 (109.75)	1/31/2011	B2BDN8	1,510
699-97-45	Horn	9.75 (32.00)	1/31/2011	B2BDP0	53.9
(C5659)		9.91 (32.50)	1/31/2011	B2BDP1	53.2
		11.09 (36.40)	1/31/2011	B2BDP2	55.6
		12.01 (39.40)	1/31/2011	B2BDP3	24.1

bgs = below ground surface

ID = identification

HEIS = Hanford Environmental Information System

In Well 699-97-45, lower Cr(VI) concentrations are present at the bottom of the aquifer. However, the analytical results only vary by a relatively small amount between depths, resulting in inconclusive results in that well. Vertical stratification of Cr(VI) was not apparent in Well 199-D5-126.

During the RI, 17 monitoring wells and 10 soil borings (5 of which were completed as temporary wells) were installed. Groundwater samples were collected during drilling at discrete depth intervals to characterize the vertical extent of contaminants. Most of the wells were completed in the unconfined aquifer; however, five wells were completed in the first water-bearing unit of the RUM.

Table 4-21 and Table 4-22 present the groundwater analytical results for total chromium and Cr(VI) by depth for the wells and boreholes drilled as part of the RI/FS field effort. As shown in Table 4-21, vertical stratification of Cr(VI) is indicated to some extent in the 100-D southern plume unconfined aquifer. Stratification is not indicated in the 100-D northern plume or the 100-H plume.

Laboratory data qualifiers are included in Tables 4-15 and 4-16, with "D" indicating a dilution factor, "U" indicating the analyte was not detected above the limiting criteria shown, and "B" indicating that the analyte concentration was near the detection limit for that test method. It should also be noted that the laboratory methods used to determine total chromium and Cr(VI) are different. Method 6010 Metals by ICP or Method 200.8 (which has a lower detection limit) is used to determine total chromium, and Method 7196, a color metric method, is used to determine Cr(VI). Method 7196 is susceptible to interference from colored matrices and chemical interference. Because of the potential for interference, as well as differences in sample preparation and analysis procedures, it is generally thought that the total

chromium methodology provides a more accurate reading than the Cr(VI) method. However, using current technology, a method is not available that provides both total chromium and Cr(VI) results. Results for individual wells and boreholes are discussed in the following paragraphs.

**100-D, Southern Plume: Unconfined Aquifer** – These wells are located within the southern plume of 100-D, where the highest concentrations of Cr(VI) have been identified. The analytical results indicate present-day vertical stratification in areas where highly concentrated sodium dichromate was handled. However, it should be noted that this stratification is not well defined or consistent in the aquifer.

Table 4-21. Chromium and Cr(VI) Sample Results from RI Drilling – 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Chromium (µg/L)	Cr(VI) (μg/L)	Turbidity (NTU)	Specific Conductance (µS/cm)
	199-D3-5 (C7620, Well 2)	27.5 to 28.1 (90.3 to 92.3)	14.4	8		
<u>.</u>		27.7 to 28.1 (90.9 to 92.3)	12.4	3.7 (U)	13.2	533
Aquifer		29.3 to 29.7 (96 to 97.4)	15.8 (D)	2 (U)	9.35	575
ped		30.8 (101.2)	48.2 (D)	27		
onfir		30.8 (101.2)	49.2 (D)	27	5.96	596
Unc		31.4 (103)	84.7 (D)	73.1	8.45	577
ne: 1	199-D5-144	28.01 (91.90)	684	703		
100-D, Southern Plume: Unconfined Aquifer	(C8668, Well R5 redrill)	28.01 (91.90)	684	636	293	727
		29.11 (95.51)	403			
		29.11 (95.51)	407		8.31	533
), So		30.27 (99.31)	304	284	19.5	535
100-I		31.49 to 31.64 (103.3 to 103.8)	257	238		
-		31.49 to 31.64 (103.3 to 103.8)	246	241	13.7	535
		32.61 (107)	103	98	302	600
1	199-D5-141 (C7625, Well R5)	27.5 (90.3)	2,070	2,010 (D)		
RUN		27.5 (90.3)	1,990 (D)	2,100	50.8	642
100-D, Southern Plume: RUM Wells		29.1 (95.5)	6,080 (D)	6,520 (D)		
		29.1 (95.5)	6,290 (D)	6,510 (D)	7.42	560
		30.6 (100.5)	5,300 (D)	5,440 (D)	4.14	536
		32.5 (106.5)	961 (D)	986	1.36	447
		34.1 (112)	2,470 (D)	2,590 (D)	24.1	432
1-00		49.5 (162.5)	1 (UD)	2 (U)	742	449
-		94.1 (308.8)	0.5 (U)	2 (U)	571	338

Table 4-21. Chromium and Cr(VI) Sample Results from RI Drilling – 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Chromium (µg/L)	Cr(VI) (μg/L)	Turbidity (NTU)	Specific Conductance (µS/cm)
	199-D5-133	26.9 (88.2)	36.9	31.1		
	(C7621, Well 3)	26.9 (88.2)	36.7 (D)	36	3.97	651
		28.3 (92.7)	16.5 (D)	2 (U)	336	596
		29.8 (97.8)	27.2 (D)	7.4		
		29.8 (97.8)	20.4 (D)	9.9	25.4	626
		31.4 (103)	22.3 (D)	2 (U)	214	624
	199-D5-132	27 (88.7)	28.9 (D)	15.5		
	(C7622, Well 4)	27 - 28.1 (88.7 - 92.3)	24.5	18	93.1	675
		29.4 (96.4)	17.5 (D)	7.1		
		29.4 (96.4)	19.7 (D)	6.9	45.8	667
		31.1 (102)	34.5 (D)	16.1	8.47	654
		32. (105)	29 (D)	9	91.6	646
	199-D6-3	28.7 (94)	22	17.6		
	(C7623, Well 5)	28.7 (94)	35.7	2 (U)	572	846
		30.2 (99)	39.9 (D)	2 (U)		
		30.2 (99)	39.2 (D)	2 (U)	166	825
_		30.9 (101.5)	37.3 (D)	8.2	121	840
Aquife	199-D5-140 (C7866, Well 9)	27.5 - 27.8 (90.2 - 91.3)	358 (D)	290	228	656
100-D, Northern Plume: Unconfined Aquifer		27.5 - 27.8 (90.2 - 91.3)	336	327		
ncor		28.7 (94.2)	540 (D)	521	8.2	654
: U		28.7 (94.2)	580 (D)	513		
um		30.2 (99)	460	425	100	657
n P		31.5 (103.3)	450 (D)	376	62.4	631
ther	199-D5-143	27.7 (91)	1,330	1,210 (D)	24.3	576
Nor	(C8375, Well 9 redrill)	27.7 (91)	1,260 (D)	••		
-D,		28.9 (95)	1,240 (D)	1,160 (D)	101	566
100		28.9 (95)	1,250 (D)	1,140 (D)		
		31.2 (102.5)	1,360 (D)	1,260 (D)	22.5	566
		31.7 (104)	1,460 (D)	1,460 (D)	13.2	557
utin	199-D8-101 (C7852,	21.9 (72)	34.1	27	0.64	727
Unconfin	Waste Site 116-DR-1&2)	21.9 (72)	35.6	27		

Table 4-21. Chromium and Cr(VI) Sample Results from RI Drilling - 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Chromium (µg/L)	Cr(VI) (µg/L)	Turbidity (NTU)	Specific Conductance (µS/cm)
	199-D5-142 (C7857, Waste Site 118-D-6)	26.5 - 27.4 (87.1 - 89.8)	80	79	12.2	161
		26.5 - 27.4 (87.1 - 89.8)	82.1	78		**
	Borehole C7850	21.5 (70.4)	33.5	23		
	(Waste Site 116-DR-9)	21.5 (70.4)	31.4	39	936	614
	Borehole C7851 (Waste Site 116-D-7)	20.3 - 21 (66.7 - 69)	33	8		
		20.3 - 21 (66.7 - 69)	18.9	11	>1,000	588
	Borehole C7855	27.8 (91.2)	151	143		
	(Waste Site 116-D-1B)	27.8 (91.2)	150	144	364	684
Vell	199-D5-134 (C7624, Well R4)	28 (92)	1,480	1,560 (D)		
M		28 (92)	1,420	1,480	10.4	584
RU		29.6 (97)	1,290 (D)	1,430		
me:		29.6 (97)	1,350 (D)	1,460	15.3	578
100-D, Northern Plume: RUM Well		31.1 (102)	1,250 (D)	1,670	35	567
		32.7 (107.3)	1,090 (D)	1,090 (D)	35.8	549
		41.3 (135.5)	12.6 (D)	12.2	32.1	462
D, N		46.9 (154)	1.31 (BD)	2 (U)	259	330
100		82 (268.9)	1.27 (BD)	2 (U)	82	389

### Notes:

- Data shown excludes soil samples collected through water extraction (WE) methods due to comparability of values.
  WE concentrations are consistently lower than from acid extraction methods. Also excluded from dataset are results reported in water units (that is, µg/L) for soil samples and "R" and "Y" flagged data.
- 2. Turbidity and conductivity were analyzed once per depth interval. Turbidity and conductivity values, which are field measurements, were tied to analytical samples where possible. Some samples were filtered.
- 3. Shaded cells indicate the sample was collected from a water-bearing unit within the RUM.
- B = Analyte was detected but the result is near the detection limit of the test method.
- D = Analyte was reported at a secondary dilution factor.
- U = Analyzed for but not detected above limiting criteria.

μS/cm = microSiemens per centimeter

NTU = nephelometric turbidity units

NS = not specified

"-" indicates analyte was not sampled for at that location.

Table 4-22. Chromium and Cr(VI) Sample Results from RI Drilling – 100-H

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs - m (ft)	Chromium (µg/L)	Cr(VI) (μg/L)	Turbidity (NTU)	Specific Conductance (µS/cm)
	199-H3-6 (C7626, Well 6)	15.2 (49.8)	14.8 (D)	2.5 (B)	3.37	473
		15.2 - 15.8 (49.8 - 51.8)	13.6	17	3.31	471
		16.4 (53.9)	11.5 (D)	2.7 (B)		
	199-H3-7	15.1 (49.5)	11.4	5.1		
	(C7627, Well 7)	15.1 (49.5)	22.2	13	65	524
		15.7 (51.6)	25.4 (D)	12.6	36.9	502
Let		15.7 (51.6)	25.1 (D)	16.1		
۱qui	199-Н6-3	14.8 (48.5)	15.4	2 (U)	9.21	621
ed A	(C7628, Well 10)	14.8 (48.5)	23 (D)	6		
nfin		16.2 (53.1)	20.1 (D)	2 (U)	159	618
nco		16.2 (53.1)	22.8 (D)	2 (U)		
Н: С		19.5 (64)	34.4 (D)	15.2	34.7	601
100-H: Unconfined Aquifer	199-H6-4	13.9 (45.7)	12.9	8.7		**
_	(C7629, Well 11)	13.9 (45.7)	13.6 (D)	9.2	2.58	477
		13.9 (45.7)	13.3 (D)	8		
		14.6 (48)	19.2 (D)	6.3	4.45	475
		16.2 (53)	14.4 (D)	6.8	5.53	478
		18.4 (60.5)	12.2 (D)	3.2 (B)	51.5	462
	199-H1-7	NS				
	(C7630, Well 12)	NS				
holes	199-H4-84 (C7860, Waste Site 116-H-6)	14.1 - 14.8 (46.2 - 48.6)	3.91	3.7 (U)		
; Boreholes		14.1 - 14.8 (46.2 - 48.6)	4.2	3.7 (U)	73.8	344
Aquifer	199-H4-83 (C7861, Waste Site 116-H7)	12.2 - 12.9 (40 - 42.3)	7.29	4		
100-H: Unconfined Aquifer,		12.2 - 12.9 (40 - 42.3)	7.58	5	43.3	466
	199-H3-11 (C7863,	16.5 (54.2)	25.3	11		
	Waste Site 118-H-6)	16.5 (54.2)	26.2	12	7.74	596
	Borehole C7862 (Waste Site	15.2 - 16 (49.9 - 52.4)	2 (U)	3.7 (U)		
	116-H-4)	15.2 - 16 (49.9 - 52.4)	2 (U)	3.7 (U)	>1,000	526
	Borehole C7864	15.1 (49.4)	6.84	3.7 (U)		4.1

Table 4-22. Chromium and Cr(VI) Sample Results from RI Drilling - 100-H

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs - m (ft)	Chromium (µg/L)	Cr(VI) (µg/L)	Turbidity (NTU)	Specific Conductance (µS/cm)
	(Waste Site 116-H-1)	15.1 (49.4)	7.54	3.7 (U)	18.3	490
IIs	199-H2-1 (C7631, Well R3)	9.2 (30.1)	7.44	2 (U)		w.w
We		9.2 (30.1)	10.1 (D)	2 (U)		
100-H: RUM Wells		9.2 (30.1)	9.06 (BD)	3.7 (U)	46.8	228
H: R		10.64 (34.9)*	8.8 (BD)	5.9	239	241
1-00		19.2 (62.9)	11.4 (D)	8.6	298	265
_		48.2 (158.3)	1 (UD)	2 (U)	13.7	360
		54.7 (179.6)	2.87 (BD)	2 (U)	79.2	356
	199-H3-9 (C7639, Well R1)	12.3 (40.4)	7.84	6		
		12.3 (40.4)	7.84 (BD)	3.7 (U)	6.88	478
		13.8 (45.2)	3.81 (BD)	3.1 (B)		
		13.8 (45.2)	3.58 (BD)	2.9 (B)	87.7	410
		14.2 (46.5)	8.85 (BD)	2 (U)	38.3	321
		20.8 (68.4)	319 (D)	287	599	259
		40.8 (134)	4.14 (BD)	2 (U)	132	332
		53.9 (177)	4.09 (BD)	2 (U)	9.74	369
	199-H3-10 (C7640, Well R2)	13.9 (45.5)	13.8	7.5		
		13.9 (45.5)	13.3 (D)	11	6.54	470
		15.2 (49.9)	10.5 (D)	3.7 (B)	2.98	451
		15.2 (49.9)	10.2 (D)	3.3 (B)	6.85	450
		16.1 (52.8)	13.1 (D)	2 (B)	914	289
		60.4 (198)	2.05 (BD)	2 (U)	>1,000	347
		68.2 (223.6)	2.32 (BD)	2 (U)	54.1	377

Notes: Data shown excludes soil samples collected through water extraction (WE) methods due to comparability of values. WE concentrations are consistently lower the acid extraction methods. Also excluded from dataset are results reported in water units (i.e.,  $\mu g/L$ ) for soil samples and "R" and "Y" flagged data.

Turbidity and conductivity were analyzed once per depth interval. Turbidity and conductivity values are field measurements. The sample may have been subsequently filtered.

Shaded cells indicate the sample was collected from a water-bearing unit within the RUM.

- \* = This depth was recorded incorrectly as 106.9 m, which is well beyond the total depth drilled of 57.6 m.
- B = Analyte was detected but the result is near the detection limit of the test method.
- D = Analyte was reported at a secondary dilution factor.
- U = Analyzed for by not detected above limiting criteria.

μS/cm = microSiemens per centimeter

NTU = nephelometric turbidity units

NS = not specified

"-" indicates analyte was not sampled for at that location.

Well 199-D3-5 (C7620, Well 2) – Cr(VI) concentrations in groundwater are greater than the state surface water quality standard of 10  $\mu g/L$  at this location. The Cr(VI) concentrations are less than total chromium as expected because Cr(VI) typically represents only a portion of the chromium oxidation states present. Cr(VI) concentrations in groundwater increase with depth up to 73.1  $\mu g/L$  at the 31.4 m (103 ft) depth, with a corresponding total chromium result of 84.7  $\mu g/L$ . This indicates that the majority of chromium at this location consists of Cr(VI). No post-installation groundwater samples were collected from this well in 2011.

Well 199-D5-144 (C8668, Well R5 redrill) – This well is located adjacent to waste site 100-D-100, which is undergoing excavation. Analytical results in this location were lower than those identified in a slightly downgradient well (199-D5-141). Groundwater sample results for both Cr(VI) and total chromium concentrations were nearly identical in this location, with results in all sample locations being well over the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) level of 48  $\mu$ g/L. The concentrations at the top of the RUM were the lowest detected in groundwater, at 103 and 98  $\mu$ g/L for total chromium and Cr(VI), respectively. No post-installation groundwater samples were collected from this well in 2011.

**100-D, Southern Plume:** RUM Well – This well extends into the RUM and groundwater samples were collected from both the unconfined aquifer and water-bearing units within the RUM.

Well 199-D5-141 (C7625, Well R5): In the unconfined aquifer, Cr(VI) concentrations are relatively high and distributed over the entire thickness. Cr(VI) concentrations ranging from 986 to 6,520 µg/L, as presented in Table 4-21. The total chromium and Cr(VI) mass in these samples are nearly equal, indicating that chromium is predominantly in the mobile hexavalent form and that little natural reduction is occurring in the unconfined aquifer at this location. Total chromium appears to be less than Cr(VI) in many of the samples throughout the depth intervals, indicating a potential error in laboratory analysis. Overall, the results suggest that the chromium in the unconfined aquifer is in a very mobile state.

This well was extended past the first water bearing unit in the RUM, to a second unit (presumed to be Ringold unit B). Groundwater samples were collected from both zones, with results presented in Table 4-21. Within both the first and second water bearing units identified in the RUM, neither total chromium nor Cr(VI) was detected. The well was screened within the first water bearing unit in the RUM, and neither total chromium nor Cr(VI) was detected in post-installation groundwater samples collected in August and October 2011.

**100-D, Northern Plume:** Unconfined Aquifer – These wells are located within the northern plume of 100-D and historically have had significantly lower Cr(VI) concentrations in groundwater than in the southern plume. However, there is also a hot spot with localized higher concentrations.

Well 199-D5-133 (C7621, Well 3) – No significant contaminant spikes are observed near the PRZ. The groundwater sample results from the upper 10 m of the 25 m (33 of the 82 ft) thick unconfined aquifer are slightly elevated, however, suggesting a shallow intrusion of contaminated groundwater within the unconfined aquifer. At a depth of approximately 27.7 m (91 ft), the soil boring log indicates that the felsic-rich material is no longer present and the silt content increases. The felsic material tends to be more alkaline and the Cr(VI) would remain in that valence state. This is consistent with the analytical results, which show lower Cr(VI) where the silt content of the geologic material increases. There appears to be some reduction to trivalent chromium in this lower portion of the aquifer. A post-installation groundwater sample collected from this well in August 2011 identified total chromium and Cr(VI) concentrations at  $12~\mu g/L$  and  $8.2~\mu g/L$ , respectively. The total chromium values are slightly lower than the 16.5~to  $36.9~\mu g/L$  detected during drilling. The post-installation results are consistent with the concentrations of Cr(VI), which ranged from  $36~\mu g/L$  to below detection during drilling activities.

Well 199-D5-132 (C7622, Well 4) – In the unconfined aquifer, Cr(VI) concentrations range from 6.9 to 18  $\mu$ g/L and total chromium values range from 17.5 to 34.5  $\mu$ g/L. Total chromium is higher than Cr(VI) in all samples, and the ratio indicates a lower mobility within the aquifer at this location, with the exception of the uppermost sample. Slightly higher Cr(VI) concentrations were detected near the top and near the bottom of the aquifer. The stratigraphic units noted in the borehole do not indicate any significant variability in lithology except for a slight increase in gravel content near the bottom of the well. A post-installation sample collected from this well in August 2011 had total chromium at 43 and 41  $\mu$ g/L, with Cr(VI) detected at 41.3  $\mu$ g/L. The total chromium and Cr(VI) concentrations are slightly higher than identified during drilling.

Well 199-D6-3 (C7623, Well 5) – In the unconfined aquifer, Cr(VI) concentrations ranged from below detection to 17.6  $\mu$ g/L at a depth of 28.7 m (94 ft) bgs, the shallowest sample depth. Laboratory results from the duplicate sample at that depth were below detection, introducing some uncertainty to the analytical results from that sample interval. Total chromium results in the unconfined aquifer ranged from 22 to 39.9  $\mu$ g/L, and are relatively consistent throughout the aquifer thickness. A post-installation groundwater sample collected from this well in August 2011 had total chromium and Cr(VI) concentrations of 10  $\mu$ g/L and 4.4  $\mu$ g/L, respectively. These values are consistent with the concentration range identified during borehole groundwater sampling activities.

Well 199-D5-140 (C7866, Well 9) – Total chromium concentrations in the unconfined aquifer during drilling ranged from 336 to 580  $\mu$ g/L, while Cr(VI) concentrations ranged from 290 to 521  $\mu$ g/L. The total chromium and Cr(VI) track closely in most samples, indicating that most of the Cr(VI) in groundwater is in the mobile hexavalent oxidation state. A post-installation groundwater sample collected from this well in June 2011 had total chromium concentrations of 372 and 375  $\mu$ g/L. The Cr(VI) concentration from the same sample date was 388  $\mu$ g/L, which is slightly higher than the total chromium level. This difference is likely within the range of laboratory error. Analytical values are consistent with the concentration range identified during borehole groundwater sampling activities. The well was decommissioned in mid-June 2011 for continued waste site remediation activities.

Well 199-D5-143 (C8375, Well 9 redrill) – In the unconfined aquifer, total chromium concentrations ranged from 1,240 to 1,460  $\mu$ g/L, while Cr(VI) concentrations ranged from1,140 to 1,460  $\mu$ g/L. The total chromium and Cr(VI) results are nearly identical, indicating that most of the chromium is in the hexavalent oxidation state and mobile. These concentrations are consistent with the location of the well in the 100-D northern plume. A post-installation groundwater sample collected from this well in August 2011 had total chromium and Cr(VI) detected at 1,420  $\mu$ g/L and 1,480  $\mu$ g/L, respectively. These values are consistent with the concentration range identified during borehole groundwater sampling activities.

100-D, Northern Plume: Unconfined Aquifer Boreholes – These boreholes were installed near selected waste sites in the 100-D northern plume. Because the boreholes were drilled primarily to determine soil conditions, they were not extended to the top of the RUM, as were the wells. It should be noted that two of these boreholes were converted to temporary wells to obtain groundwater samples because of low water production within the borehole at the time of drilling.

Temporary Well 199-D8-101 (C7852, Waste Site 116-DR-1&2) – Groundwater samples were collected from one location during drilling, the upper 1.5 m (5 ft) of the unconfined aquifer. Samples from that location were analyzed as duplicates with results being nearly identical. Total chromium concentrations were detected at about 35  $\mu$ g/L and Cr(VI) concentrations were at 27  $\mu$ g/L, indicating that the chromium in the unconfined aquifer at this location is primarily in the mobile Cr(VI) state. Three post-installation groundwater samples were collected from this well in 2011, with samples collected in April, June, and July. Total chromium concentrations showed a decreasing trend from April through July (64  $\mu$ g/L,

53  $\mu$ g/L, and 13  $\mu$ g/L, respectively). Cr(VI) concentrations also showed a similar decreasing trend from April through July (61  $\mu$ g/L, 50  $\mu$ g/L, and 9  $\mu$ g/L, respectively). The decreasing concentrations can be attributed to pump-and-treat system operations. The previous borehole total chromium and Cr(VI) groundwater results fall in the middle of the post-installation results.

Temporary Well 199-D5-142 (C7857, Waste Site 118-D-6) – Groundwater samples were collected in the upper 1.5 m (5 ft) of the unconfined aquifer. The duplicate samples had total chromium at concentrations of 80 and 82.1  $\mu$ g/L and Cr(VI) concentrations were at 79 and 78  $\mu$ g/L, indicating that the chromium in the unconfined aquifer at this location is primarily in the mobile Cr(VI) state. A post-installation groundwater sample collected from this well in April 2011 had total chromium and Cr(VI) detected at 21.6  $\mu$ g/L and 16  $\mu$ g/L, respectively. These values are approximately four times lower than previously identified during borehole groundwater sampling activities and are attributed to the nearby extraction and injection wells.

Borehole C7850 (Waste Site 116-DR-9) – Groundwater samples were collected from the upper 1.5 m (5 ft) of the unconfined aquifer. Total chromium was detected at 31.4 and 33.5  $\mu$ g/L and Cr(VI) was detected at 23 and 39  $\mu$ g/L, indicating that the chromium in the aquifer at this location is primarily in the mobile Cr(VI) state.

Borehole C7851 (Waste Site 116-D-7) – Groundwater samples were collected from the upper 1.5 m (5 ft) of the unconfined aquifer. Total chromium was detected at 18.9 to 33  $\mu$ g/L, while Cr(VI) was detected at 8 to 11  $\mu$ g/L. The duplicate sample results for total chromium were not as similar as would be expected for water samples, introducing some uncertainty in the data quality. The lithology identified in the borehole log did not indicate any conditions affecting sample collection. The values of Cr(VI) at this location are considered more accurate.

Borehole C7855 (Waste Site 116-D-1B) – Groundwater samples were collected from the upper 1.5 m (5 ft) of the unconfined aquifer. Samples from that location were analyzed as duplicates with concentrations being nearly identical. Total chromium concentrations were reported at 150 and 151  $\mu$ g/L, and Cr(VI) concentrations were reported at 143 and 144  $\mu$ g/L. This indicates that the chromium in the aquifer at this location is primarily in the mobile Cr(VI) state.

100-D, Northern Plume: RUM Well – This well extends into the first water-bearing unit in the RUM and groundwater samples were collected from both the unconfined aquifer and water-bearing units within the RUM.

199-D5-134 (C7624, Well R4) – In the unconfined aquifer, Cr(VI) concentrations are relatively high and uniformly distributed over the entire thickness of the aquifer. Concentrations of total chromium in groundwater decrease from values of 1,480  $\mu$ g/L near the top of the unconfined aquifer to 1,090  $\mu$ g/L at the surface of the RUM. The Cr(VI) concentrations range from 1,090 to 1,670  $\mu$ g/L, with concentrations decreasing below the base of the unconfined aquifer, which is approximately 40 m (131 ft) bgs. The total chromium and Cr(VI) mass are nearly equal, indicating that chromium is predominantly in the mobile hexavalent form and that little natural reduction is occurring in the aquifer at this location. Total chromium was reported as less than Cr(VI) from samples at a depth of about 31 m (100 ft), indicating a potential error in laboratory analysis, or matrix interference.

At this well location, the RUM was encountered at 33.1 m (108.5 ft) bgs. Three samples were collected for laboratory analysis from water-bearing units within the RUM. Total chromium and Cr(VI) were both detected from the first water-bearing unit, with a concentration of 12.6 and 12.2  $\mu$ g/L, respectively. An evaluation of the boring logs and daily reports indicates that the sample was collected following difficulty during drilling, resulting in a delay in sample collection of more than two days. Because the well drilling was not yet completed, and high concentrations (1,090  $\mu$ g/L) of total chromium and Cr(VI)

were detected in the aquifer above the RUM surface, it is possible that this sample was contaminated from groundwater originating in the unconfined aquifer. Two additional lower groundwater samples were collected within the RUM, presumably including the Ringold unit B, and neither total chromium or Cr(VI) was detected. The first water-bearing unit in the RUM was screened to allow for future sampling from that unit.

**100-H:** Unconfined Aquifer – These wells are located within 100-H and screened in the unconfined aquifer. The Cr(VI) concentrations in the unconfined aquifer at 100-H have been significantly lower than in 100-D, but remain higher than those found in the Horn area.

199-H3-6 (C7626, Well 6) – Total chromium concentrations in the unconfined aquifer were relatively consistent with depth. Concentrations of Cr(VI) show some variability and range from 2.5 to 17  $\mu$ g/L at the same location. Two separate laboratories analyzed the sample by the same analytical method and reported considerably different results, with the higher results (17  $\mu$ g/L) being reported for the filtered sample, which is typically considered more reliable and usually lower than results from unfiltered samples, where 2.5  $\mu$ g/L was reported. No post-installation groundwater samples were collected from this well in 2011.

199-H3-7 (C7627, Well 7) – Total chromium concentrations in groundwater ranged from 11.4 to 25.4  $\mu$ g/L at this well. Cr(VI) concentrations are less than total chromium as expected, ranging from 5.1 to 16.1  $\mu$ g/L. The exception is the filtered sample pair where Cr(VI) was higher (13  $\mu$ g/L) than the total chromium value (11.4)  $\mu$ g/L. Two separate laboratories analyzed one sample from the same location and reported considerably different results, with the higher results (13  $\mu$ g/L) being reported for the filtered sample, which is typically considered more reliable and usually lower than results from unfiltered samples, where 5.1  $\mu$ g/L was reported. No post-installation groundwater samples were collected from this well in 2011.

199-H6-3 (C7628, Well 10) – Total chromium concentrations in groundwater range from 15.4 to 34.4  $\mu$ g/L, with values for Cr(VI) less than total chromium as expected, ranging from undetected up to 15.2  $\mu$ g/L. The highest Cr(VI) reported at this well (15.2  $\mu$ g/L) was collected from the bottom of the unconfined aquifer, approximately 2.3 m (7.5 ft) below the previous sample depth. No post-installation groundwater samples were collected from this well in 2011.

199-H6-4 (C7629, Well 11) – Total chromium concentrations in groundwater range from 12.2 to 19.2  $\mu g/L$ , with values for Cr(VI) less than total chromium as expected, ranging from 3.2 to 9.2  $\mu g/L$ . Cr(VI) appears to be uniformly distributed through the entire thickness of the aquifer. In contrast to Well 199-H6-3 (C7628, Well 10), the lowest Cr(VI) in groundwater reported at this well (3.2  $\mu g/L$ ) was collected from the bottom of the unconfined aquifer, approximately 3.3 m (10.8 ft) below the previous sample depth. No post-installation groundwater samples were collected from this well in 2011.

199-H1-7 (C7630, Well 12) – Total chromium and Cr(VI) concentrations in groundwater had similar concentrations. The two results presented for total chromium are 16  $\mu$ g/L and 14  $\mu$ g/L; however, both results are "B" flagged, indicating the result was close to the detection limit for the test method, accounting for the variability. A post-installation groundwater sample collected from this well in August 2011 had total chromium and Cr(VI) detected at 16  $\mu$ g/L and 14  $\mu$ g/L, respectively. These values are consistent with the concentration range identified during borehole groundwater sampling activities.

**100-H: Vadose Zone Boreholes** – These boreholes were installed near selected waste sites in 100-H. Because the boreholes were drilled primarily to evaluate contaminant concentrations in the vadose zone, they were only drilled into the top of the aquifer. Three of these boreholes were converted to temporary wells screened in approximately 1.5 m (5 ft) into the aquifer to obtain groundwater samples.

199-H4-84 (C7860, Waste Site 116-H-6) – Total chromium concentrations in groundwater are approximately 4  $\mu$ g/L, with Cr(VI) not detected. The duplicate sample results are nearly identical.

A post-installation groundwater sample collected from this well in June 2011 had total chromium and Cr(VI) detected at 28.6  $\mu g/L$  and 25  $\mu g/L$ , respectively. The total chromium and Cr(VI) concentrations are higher than previously identified in borehole groundwater samples. It is not known what caused this increase, but this well will continue to be monitored.

199-H4-83 (C7861, Waste Site 116-H7) – Total chromium was detected in groundwater at 7.3 and 7.6  $\mu$ g/L, with Cr(VI) concentrations of 4 and 5  $\mu$ g/L. The duplicate sample results are essentially the same. A post-installation groundwater sample collected from this well in June 2011 had total chromium and Cr(VI) detected at 8.3  $\mu$ g/L and 6  $\mu$ g/L, respectively. These values are consistent with the concentration range identified during borehole groundwater sampling activities.

199-H3-11 (C7863, Waste Site 118-H-6) – Total chromium was detected at 25.3 and 26.2  $\mu$ g/L, with Cr(VI) concentrations of 11 and 12  $\mu$ g/L. The Cr(VI) concentrations are less than total chromium. This is expected where Cr(VI) represents a single oxidation state within the total chromium concentration present. A post-installation groundwater sample collected from this well in June 2011 had total chromium and Cr(VI) concentrations of 6.6  $\mu$ g/L and 4  $\mu$ g/L, respectively. These values are lower than previously identified during borehole groundwater sampling activities.

**Borehole C7862 (Waste Site 116-H-4)** – Concentrations of both Cr(VI) and total chromium were below detection limits.

**Borehole C7864 (Waste Site 116-H-1)** – Total chromium concentrations were reported at 7.5 and 6.8 μg/L. The Cr(VI) concentrations were below detection limits.

**100-H: RUM Wells** – These wells extend into the RUM and groundwater samples were collected from both the unconfined aquifer and lower water-bearing units within the RUM.

199-H2-1 (C7631, Well R3) – In the unconfined aquifer, Cr(VI) concentrations are below the detection limit at all depth intervals except for at the RUM surface. The sample at the bottom of the unconfined aquifer had a Cr(VI) concentration of 5.9  $\mu$ g/L. Total chromium concentrations in the unconfined aquifer range from 7.44 to 10.1  $\mu$ g/L, with the analytical results flagged as near the detection limit in two of the samples.

Total chromium and Cr(VI) were detected in the first water-bearing unit in the RUM at 11.4  $\mu$ g/L and 8.6  $\mu$ g/L, respectively. Concentrations in samples collected from deeper water-bearing units were below the detection limits for both total chromium and Cr(VI). Neither total chromium nor Cr(VI) was detected in a post-installation groundwater sample collected from the first water-bearing unit in August 2011. Given the low levels detected during drilling, some variation in concentrations is not unexpected. Additional sampling will be needed to determine if low levels of Cr(VI) and total chromium are present in that location.

199-H3-9 (C7639, Well R1) – Total chromium concentrations in the unconfined aquifer range from 3.58  $\mu$ g/L to 8.85  $\mu$ g/L, with no discernible vertical pattern to the concentration distribution observed. The Cr(VI) concentrations in the unconfined aquifer range from below detection to 6  $\mu$ g/L; however, the sample with a result of 6  $\mu$ g/L was a duplicate to a sample that reported nondetectable concentrations. The higher result was reported for the unfiltered sample, which can have interference from the presence of color or chemicals in groundwater. The filtered sample result is considered more representative of conditions.

The groundwater sample collected from the first water-bearing unit of the RUM had total chromium and Cr(VI) detected at 319  $\mu$ g/L and 287  $\mu$ g/L, respectively. This sample represents borehole water during drilling and, therefore, the high contaminant concentrations may be caused by high turbidity values (599 nephelometric turbidity units [NTU]) present during sampling. A groundwater sample collected in

August 2011 had Cr(VI) detected at 115  $\mu$ g/L, which is likely to be more representative of aquifer conditions, because the sample was collected from a completed monitoring well. This result confirms the presence of high levels of Cr(VI) in the first water-bearing unit of the RUM.

Within the next two water-bearing units of the RUM, the total chromium concentrations in groundwater were significantly lower. Concentrations for the two lower water-bearing units were reported at approximately 4  $\mu$ g/L. The results were flagged by the laboratory as being estimated values. The corresponding Cr(VI) concentrations in groundwater were below detection limits.

199-H3-10 (C7640, Well R2) – Total chromium concentrations in the unconfined aquifer range from  $10.2~\mu g/L$  to  $13.8~\mu g/L$ , with no discernible vertical concentration trends observed. The Cr(VI) concentrations in the unconfined aquifer range from 2 to  $11~\mu g/L$ , with slightly lower concentrations distributed in deeper portions of the unconfined aquifer. Total chromium and Cr(VI) concentrations in groundwater samples from the first water-bearing unit of the RUM and two deeper water-bearing units were less than their respective detection limits. No post-installation groundwater samples have been collected from this well in 2011.

Key to understanding potential vertical stratification of Cr(VI) is an understanding of the underlying geology and evaluating the concentration patterns in relation to that geology. Localized variations in stratigraphy often result in different contaminant distribution trends. The geologic features and associated Cr(VI) concentrations are presented on Figures 4-91 through 4-96. The cross-section locations are presented on Figure 4-91.

Cross-section A to A' (Figure 4-92) transects the southern plume at 100-D. As presented in Tables 4-15 and 4-16, vertical Cr(VI) stratification in the unconfined aquifer appears to be present beneath 100-D where high concentrations of 70 percent sodium dichromate solution was handled during reactor operations. However, concentrations are not consistently increasing or decreasing with depth across 100-D/H. A trend toward some vertical stratification is most prominent in the unconfined aquifer at RI Well 199-D3-5 (Table 4-21), not shown on the cross-section. At Well 199-D3-5, Cr(VI) concentrations increase with depth to the surface of the RUM.

At Well 199-D5-141 (C7625, Well R5), high concentrations of Cr(VI) are present in the unconfined aquifer; however, a Cr(VI) stratification trend was not observed. The Cr(VI) concentrations are elevated at several mid-level depths within the aquifer. Concentrations decline to 986  $\mu$ g/L at 32.46 m (106.5 ft), but rise to 2,590  $\mu$ g/L at the RUM surface, where a depression exists. As shown on cross-section A to A', the Cr(VI) concentrations from the first water-bearing unit in the RUM and the lower water-bearing units were below detection limits. Therefore, Cr(VI) is limited to the unconfined aquifer in this location.

As shown in cross-section B to B' (Figure 4-93) and Table 4-21, vertical Cr(VI) stratification in the unconfined aquifer is not apparent in the 100-D northern plume. An area of higher Cr(VI) concentrations is observed in the unconfined aquifer at Wells 199-D5-134 (C7624, Well R4), 199-D5-126, 199-D5-143 (C8375, Well 9 redrill), and 199-D5-140 (C7866, Well 9). A slight depression in the RUM is also present in this area and appears to extend farther toward the river than at cross-section A to A', with a gentle topographical rise in the RUM surface that appears to impede contaminant transport in this location.

RI Well 199-D5-134 was drilled into the lower water-bearing units of the RUM to evaluate the vertical extent of Cr(VI) beneath the northern plume. A concentration of 12.2  $\mu$ g/L Cr(VI) was detected during drilling from the first water-bearing unit in the RUM. The well was screened across this stratigraphic unit during completion and a laboratory result from a post-installation sample, collected on January 30, 2012, was below the detection limits. In addition, samples collected from the lower water-bearing units did not have Cr(VI) detected.

At cross-section C to C', which is located in 100-D parallel to the river, the variation in the RUM surface is apparent (Figure 4-94). However, few vertical profile samples have been collected. Existing sampling results along this cross-section do not indicate stratification in Cr(VI) with depth.

Cross-section D to D' (Figure 4-95) provides a transect from 100-D through the Horn area to 100-H. Based on both historical and recent vertical sampling in the unconfined aquifer, Cr(VI) stratification is limited across the Horn. Concentrations of Cr(VI) along this cross-section are generally below 100  $\mu$ g/L, except at 100-D, with many wells having concentrations below the DWS of 48  $\mu$ g/L.

Cr(VI) has been detected in the first water-bearing unit of the RUM in wells located in the Horn at concentrations below the DWS. The presence of Cr(VI) in the RUM in this area is likely the result of the high hydraulic head conditions during reactor operations at 100-D forcing contaminants and water into the RUM, considered an aquitard, which is by definition able to transmit limited amounts of water between geologic units. To the east of Well 699-97-48C, Cr(VI) concentrations within the RUM diminish to below detection. This indicates that the influence of 100-D operations did not extend to 100-H within the RUM.

Cross-section E to E' (Figure 4-96) runs parallel to the Columbia River along 100-H. As shown on the cross-section, the unconfined aguifer in this area is thinner than at 100-D. There is minimal Cr(VI) stratification at 100-H, and Cr(VI) concentrations in the unconfined aguifer are generally below the DWS. Within the RUM, Cr(VI) has been identified in the first water-bearing unit but not in the lower water-bearing units. Low levels of Cr(VI) were detected in Well 199-H2-1, with concentrations during drilling of 3.7 µg/L (flagged as below detection limit), 5.9 µg/L and 8.6 µg/L at depths of 9.17, 10.64, and 19.17 m (30.1, 34.9, and 62.9 ft) bgs, respectively. Following completion, an analytical sample collected on August 17, 2011, was below the detection limits. Well 199-H2-1 delineates the northern edge of the Cr(VI) plume within the RUM. Concentrations farther south were detected at levels up to 287 μg/L (during drilling) in Well 199-H3-9. The high concentrations near the river are likely related to reactor operations, with the high head conditions associated with the nearby 116-H-7 Retention Basin overcoming an upward hydraulic gradient of the confined aquifer and forcing contaminated water into the first water-bearing unit of the RUM. These higher Cr(VI) concentrations were not detected in the RUM to the west of an apparent ridgeline trending parallel to the river, which is located slightly west of the retention basins. Concentrations in Well 199-H3-2C, west of the "ridge," are typically between 50 and 80 μg/L. The extent of contamination in the first water-bearing unit of the RUM is not delineated to the south, but appears to follow the area of downward RUM surface slope along the river.

Deeper water bearing units, such as those within the Ringold Formation unit B, the Ringold Formation lower mud, and the basalt units are also presented in cross sections A-A', B-B', D-D', and E-E'. Concentrations in these lower units are consistently below 10 µg/L.

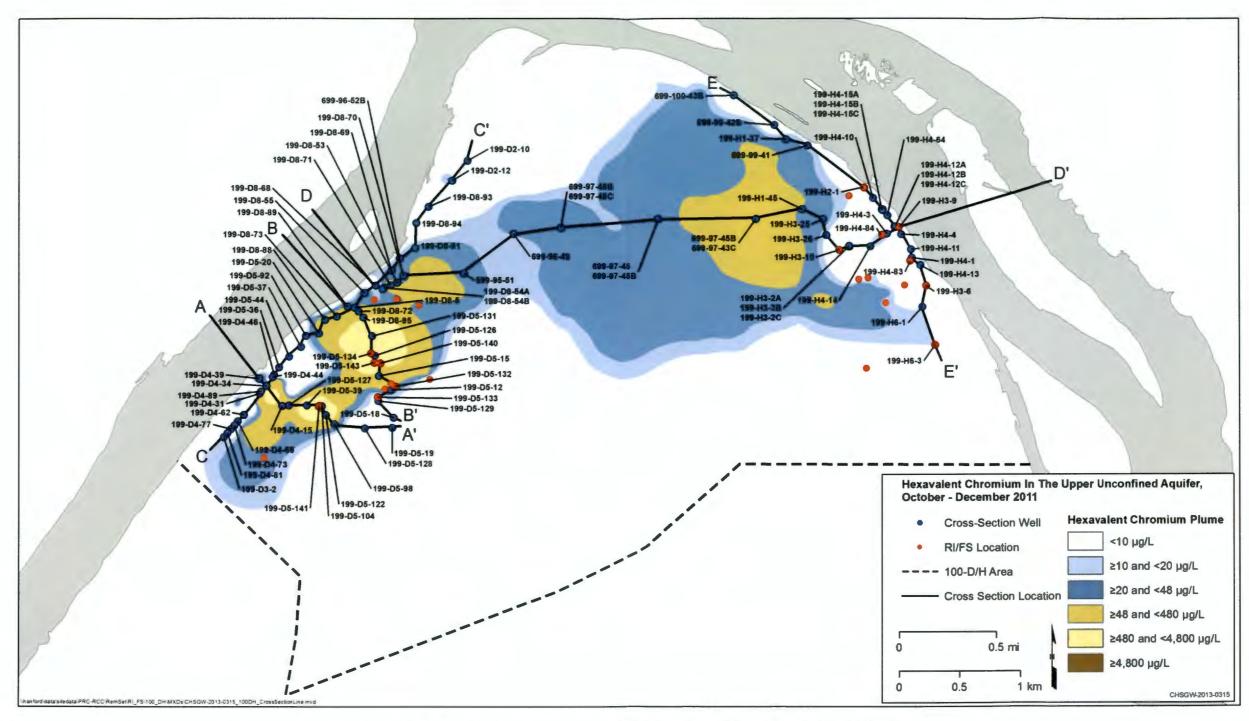


Figure 4-91. Trendline Location Map for 100-D/H Hydrogeologic Cross Sections and RI Wells

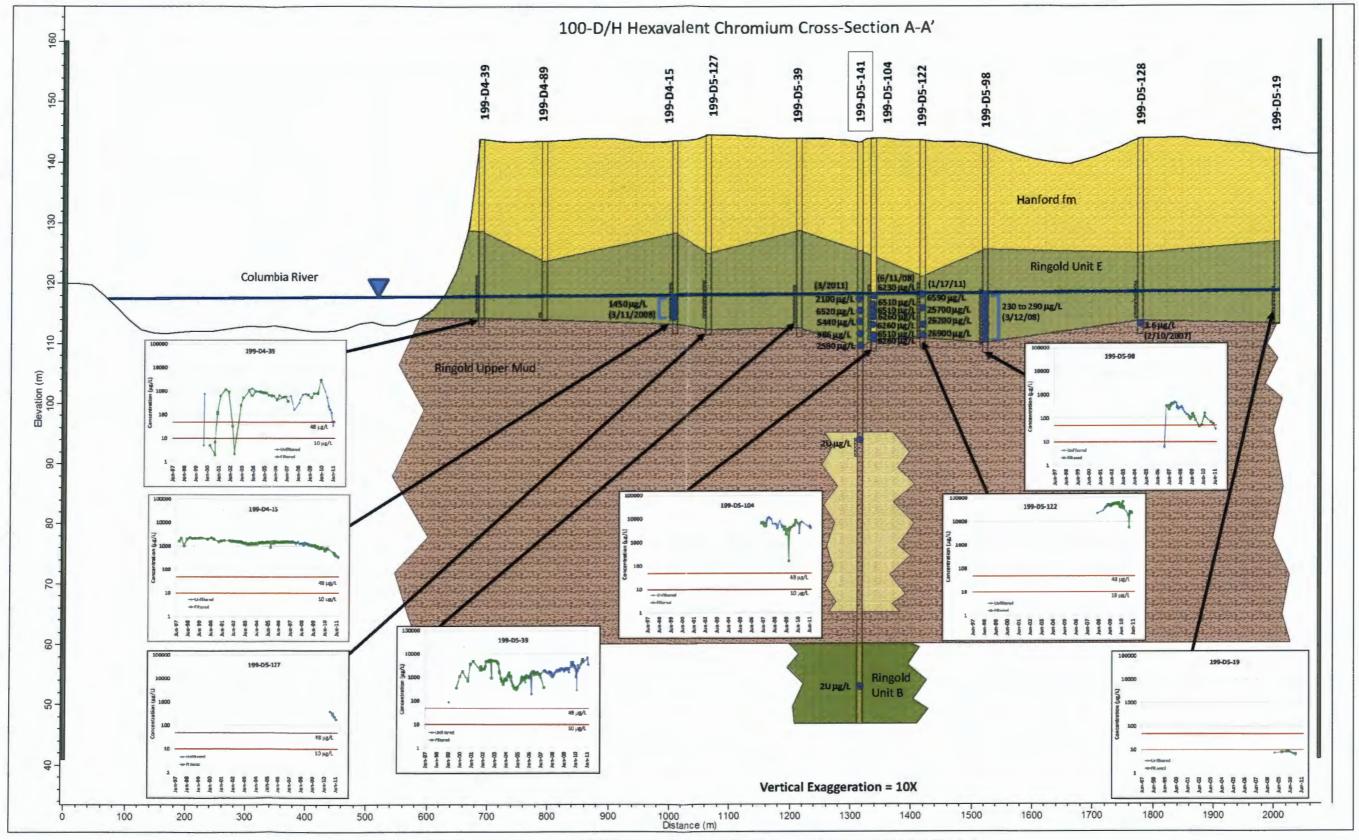


Figure 4-92. Vertical Distribution of Cr(VI) Concentrations in Groundwater shown on Cross-Section A-A'

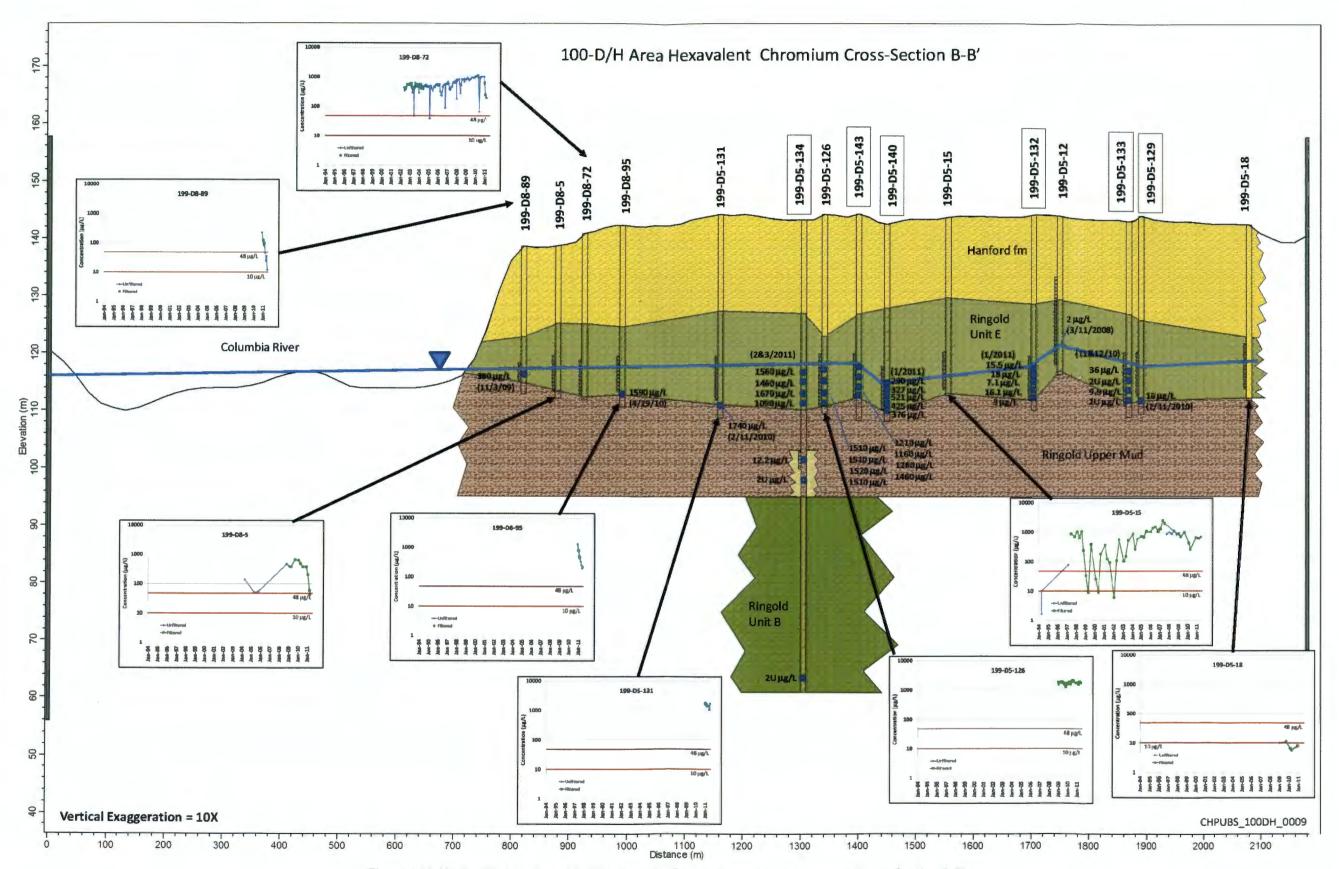


Figure 4-93. Vertical Distribution of Cr(VI) Concentrations in Groundwater shown on Cross-Section B-B'

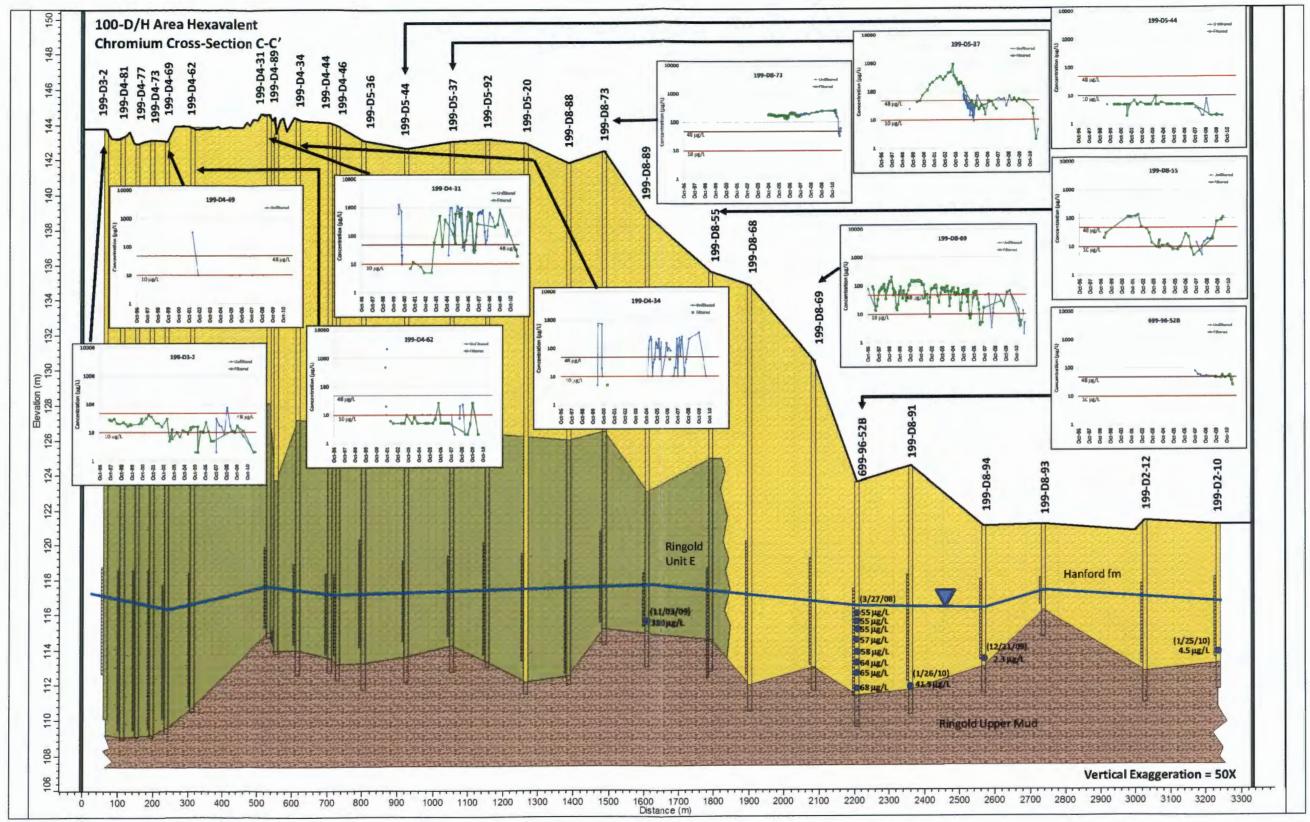


Figure 4-94. Vertical Distribution of Cr(VI) Concentrations in Groundwater shown on Cross-Section C-C'

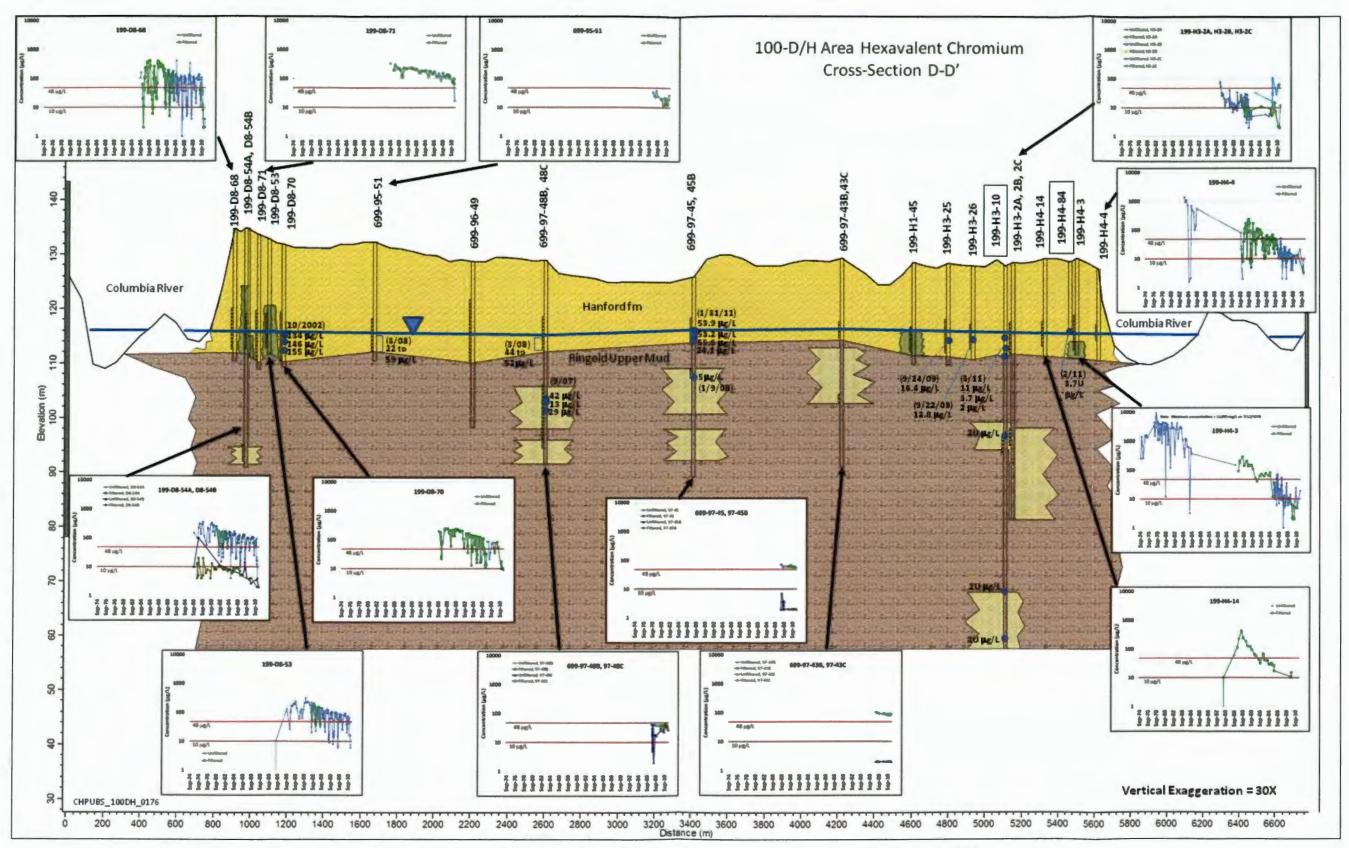


Figure 4-95. Vertical Distribution of Cr(VI) Concentrations in Groundwater shown on Cross-Section D-D'

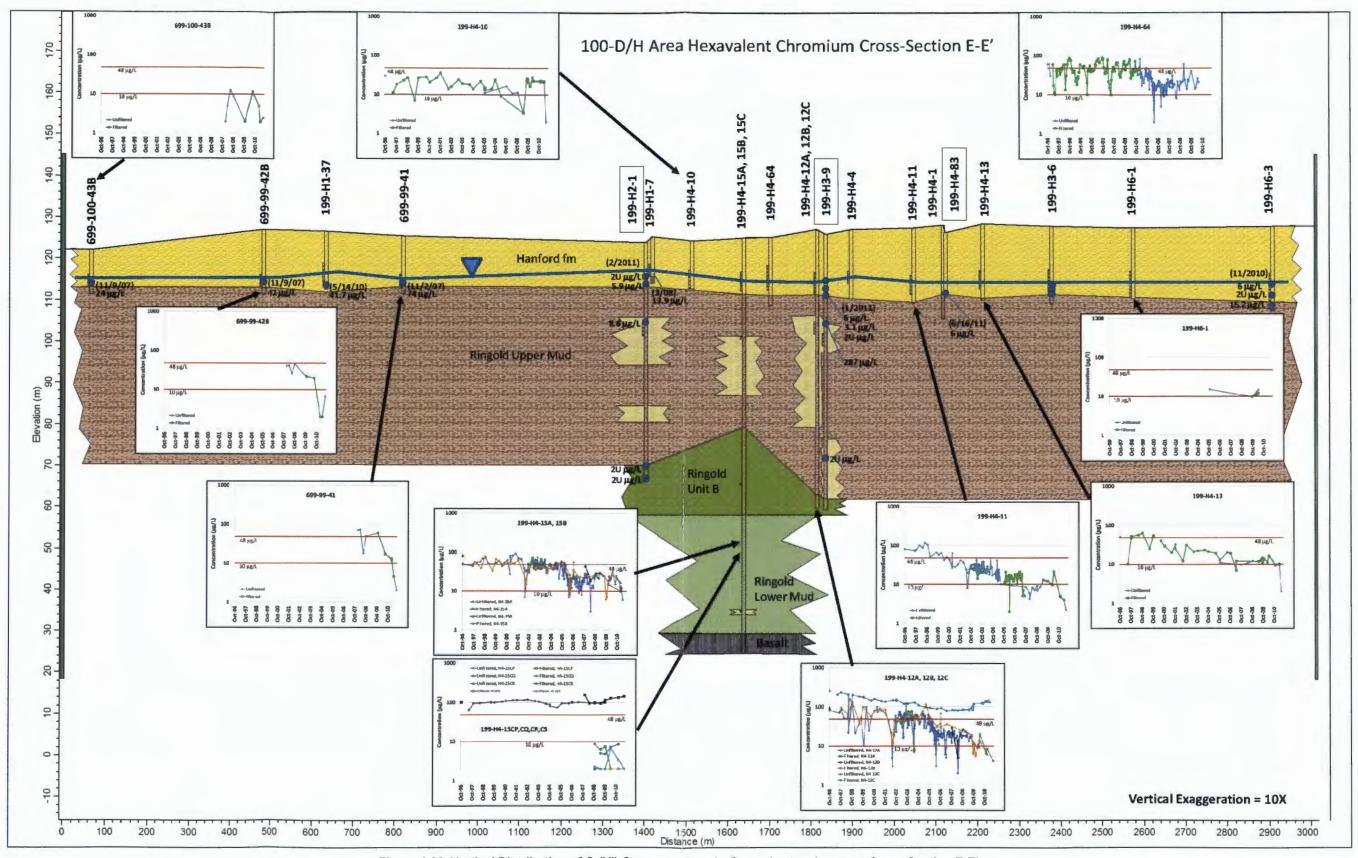


Figure 4-96. Vertical Distribution of Cr(VI) Concentrations in Groundwater shown on Cross-Section E-E'

#### 4.5.3 Nitrate

Nitrate may be expressed as nitrate (NO<sub>3</sub>) or as nitrate-nitrogen (NO<sub>3</sub>-N). The DWSs for NO<sub>3</sub>-N and NO<sub>3</sub> are 10,000 and 45,000 µg/L, respectively. Nitrate is present in the unconfined aquifer at concentrations exceeding the 45,000 µg/L DWS, primarily in 100-D (Figure 4-97). Nitrate concentrations in groundwater in the Horn are below the DWS, and a small area in 100-H near the 183-H Solar Evaporation Basin exceeds the DWS. Nitrate has not been detected in the water-bearing units of the RUM. Aquifer tube concentrations during 2011 were below the DWS in 100-D/H. EPA has not identified a water quality criterion, nor has the State of Washington promulgated a surface water quality standard for nitrate. A no effect threshold value of 199 mg/L has been identified for nitrate. As a result, nitrate concentrations measured in aquifer tubes were compared to the DWS. The primary source of nitrate in 100-D/H is nitric acid used during reactor operations as a decontamination solution. Nitric acid and other decontamination solutions were disposed in cribs, trenches, and French drains near the building where they were used. These solutions were also occasionally combined with reactor cooling water and discharged to the river (100-D Area Technical Baseline Report [WHC-SD-EN-TI-181]). Another reactor operation related source is from oxidation of ammonia discharged in the condensate solution. Secondary contributors include septic systems, sewer lines, and former agricultural practices.

**100-D.** Within the unconfined aquifer underlying 100-D, nitrate is present in two general areas, with most of the plume area slightly above the DWS. Nitrate concentrations in groundwater from the southern plume extraction wells (199-D5-39 and 199-D5-104) are currently stable near 45,000 μg/L. However, because of the startup of the DX pump-and-treat system in December 2010, previously identified trends in the remaining portion of the plume are no longer apparent. For example, Well 199-D4-15, which is located between two extraction wells, had stable values around 60,000 μg/L. Concentrations subsequently decreased to 44,300 μg/L in April 2011, the first monitoring event following the DX system startup. At the north end of the ISRM barrier, nitrate concentrations in Well 199-D5-36 increased sharply from 5,000 μg/L in 2010 to 46,500 μg/L in August 2011. Nitrate concentrations in groundwater from other areas of the southern portion of the plume are also fluctuating, with concentrations actually increasing in some locations (199-D5-17) in response to changes in the groundwater flow regime.

Figure 4-98 shows seasonal variation in nitrate concentrations in the unconfined aquifer (100-D southern plume wells) during fall and spring 2011. Nitrate concentrations in groundwater were greater in fall 2009 than in spring 2010 in 20 wells (77 percent). Since the startup of the DX pump-and-treat system, the seasonal variation patterns are not as consistent.

Groundwater from the northern plume extraction wells (199-D5-20, 199-D8-53, 199-D8-68, and 199-D8-54A) have nitrate concentrations that are generally stable or increasing slightly and often exhibit seasonal variation (with lowest concentrations in the spring). Nitrate concentrations in the unconfined aquifer exceed the DWS in fall sampling rounds in Well 199-D8-72, but are often below the DWS in spring rounds. A sample collected from 199-D8-72 in March 2011 had a result below the DWS, at the lowest concentration observed in this well (21,800 µg/L).

Concentrations of nitrate in northern plume monitoring wells 199-D5-14, 199-D5-13, and 199-D8-4 are above the DWS, but are either stable or decreasing through the end of 2011. During 2012, concentrations in Well 199-D5-14 decreased from  $64,200~\mu g/L$  at the end of 2011 to  $43,600~\mu g/L$  at the end of 2012. With the exception of samples collected during spring, most wells in the northern plume have concentrations above  $45,000~\mu g/L$ . The effect of the DX pump-and-treat system in the northern plume has not resulted in dramatic changes in nitrate concentrations in most locations, with a few exceptions. In October 2011, a dramatic decrease in concentration was observed in the groundwater sample from Well 199-D8-5. Overall, the plume appears to have migrated farther north than previously delineated. This is likely a result of the extraction wells to the north, which are focused on Cr(VI) removal.

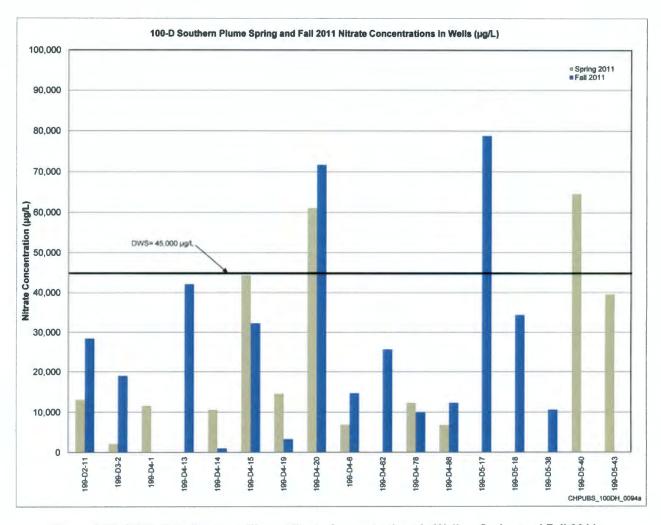


Figure 4-97. 100-D Area Southern Plume Nitrate Concentrations in Wells – Spring and Fall 2011

Of the RI wells installed at 100-D, nine were sampled for nitrate as required in the SAP. Groundwater samples from all nine wells had nitrate concentrations above the 45,000  $\mu$ g/L DWS at various depths. Within the unconfined aquifer, maximum concentrations ranged from 51,400  $\mu$ g/L at Well 199-D5-141 (C7625, Well R5) to 81,000  $\mu$ g/L at Well 199-D5-133 (C7621, Well 3). Monitoring Well 199-D5-141 also had the lowest nitrate concentration detected in the RI wells, with a result of 28,400  $\mu$ g/L detected at a depth of 34.1 m (112 ft). Figure 4-99 shows maximum nitrate concentrations in the RI wells at 100-D/H, and Table 4-23 presents the analytical results from samples collected at discrete depths during drilling. The four RI aquifer tubes at 100-D (C7645, C7646, C7647, and C7648) are located southwest of the ISRM Barrier and had nitrate concentrations less than 10,000  $\mu$ g/L, well below the 45,000  $\mu$ g/L DWS.

Monitoring wells screened in the first water-bearing unit of the RUM include one previously existing well and two RI wells: Wells 199-D8-54B, 199-D5-134 (C7624, Well R4), and 199-D5-141 (C7625, Well R5). Concentrations in groundwater samples from the first water-bearing unit in the RUM were below 10,000 µg/L, well below the DWS, in each location.

In summary, nitrate concentrations in the unconfined aquifer exceed the DWS of  $45,000~\mu g/L$ , primarily within two areas of 100-D. These areas are located near the reactors and generally coincide with the 100-D north and south Cr(VI) plumes, indicating they are derived from nitric acid and septic sources associated with 105-D and 105-DR operations, as presented in Chapter 1 and shown on Figure 1-20.

Nitrate was detected in groundwater at very low concentrations (much less than DWS) in the first water-bearing unit of the RUM.

Horn Area. Underlying the Horn, nitrate concentrations in the unconfined aquifer are well below the DWS of 45,000  $\mu$ g/L. It should be noted that in *Hanford Site Groundwater Monitoring Report for 2011* (DOE/RL-2011-118), the nitrate plume in Figure 2.5-15 indicates a small plume at Well 199-H1-27, an extraction well. The data point was considered suspect, but was included pending evaluation. The subsequent evaluation indicated an error in reporting from the laboratory. The actual concentration from that sample was 13,900  $\mu$ g/L, and the data has since been corrected.

Figure 4-100 shows seasonal variation in nitrate concentrations in the unconfined aquifer of the Horn during fall and spring 2011. However, most wells in that area were only sampled once in 2011. Nitrate concentrations in groundwater samples from wells screened in the first water-bearing unit of the RUM (699-97-43C, 699-97-45B, and 699-97-48C) are well below the DWS.

100-H. Figure 4-97 shows the nitrate plume in the unconfined aquifer at 100-D/H. Nitrate concentrations in the unconfined aquifer above the DWS of 45,000 μg/L are found in an isolated area at 100-H. It should be noted that in *Hanford Site Groundwater Monitoring Report for 2011* (DOE/RL-2011-118), the nitrate plume in Figure 2.5-15 indicates a small plume at Well 199-H4-75, an extraction well located to the west of the 100-H Area. The data point was considered suspect, but was included pending evaluation. The subsequent evaluation indicated an error in reporting from the laboratory. The actual concentration from that sample was 33,500 μg/L, and the data has since been corrected. Groundwater samples from Well 199-H4-3, located downgradient from the 183-H Solar Evaporation Basin, have a history of elevated nitrate concentrations, with a maximum concentration exceeding 3,000,000 μg/L in 1986. Concentrations were consistently below the DWS in 2008 through 2010, but increased to 72,200 μg/L in October 2011. A seasonal fluctuation is indicated in this location and supported by the fluctuation found at Well 199-H4-12A. In 2012, this fluctuation was pronounced with concentrations ranging from 2,090 μg/L in May to 58,900 μg/L in November.

Nitrate levels south of the solar evaporation basin and near the 105-H Reactor have historically been above the DWS in a couple wells (199-H4-46 and 199-H3-7). Concentrations in this area have been decreasing over time, and have been below the DWS since 2001.

Groundwater samples collected during RI drilling activities show that nitrate concentrations did not vary significantly with depth in the unconfined aquifer. Nitrate concentrations in groundwater samples from the first water-bearing unit in the RUM are much lower (less than DWS) than in the unconfined aquifer. Figure 4-99 shows the maximum nitrate concentrations in groundwater samples collected from RI wells.

Nitrate concentrations in groundwater from 100-H Area aquifer tubes are generally low, excluding several aquifer tubes downstream from the operational area, where historical concentrations slightly exceeded the DWS. In February 2011, groundwater samples from aquifer tubes 50-M and 51-M had nitrate concentrations of 37,000 and 35,900  $\mu$ g/L, respectively. A borehole groundwater sample from RI Well 199-H6-3 had 44,300  $\mu$ g/L of nitrate detected during drilling. This well is located to the west of aquifer tube 51-M, indicating that the nitrate plume extends farther to the southwest than previously interpreted.

Figure 4-101 presents the fall and spring 2011 nitrate concentrations in the unconfined aquifer underlying 100-H. Some seasonal variation in concentrations is expected at 100-H; however, wells were not sampled for nitrate in timeframes adequate to show variation. In fall 2009, nitrate concentrations were greater than spring 2010 concentrations in 11 (58 percent) of the 100-H wells.

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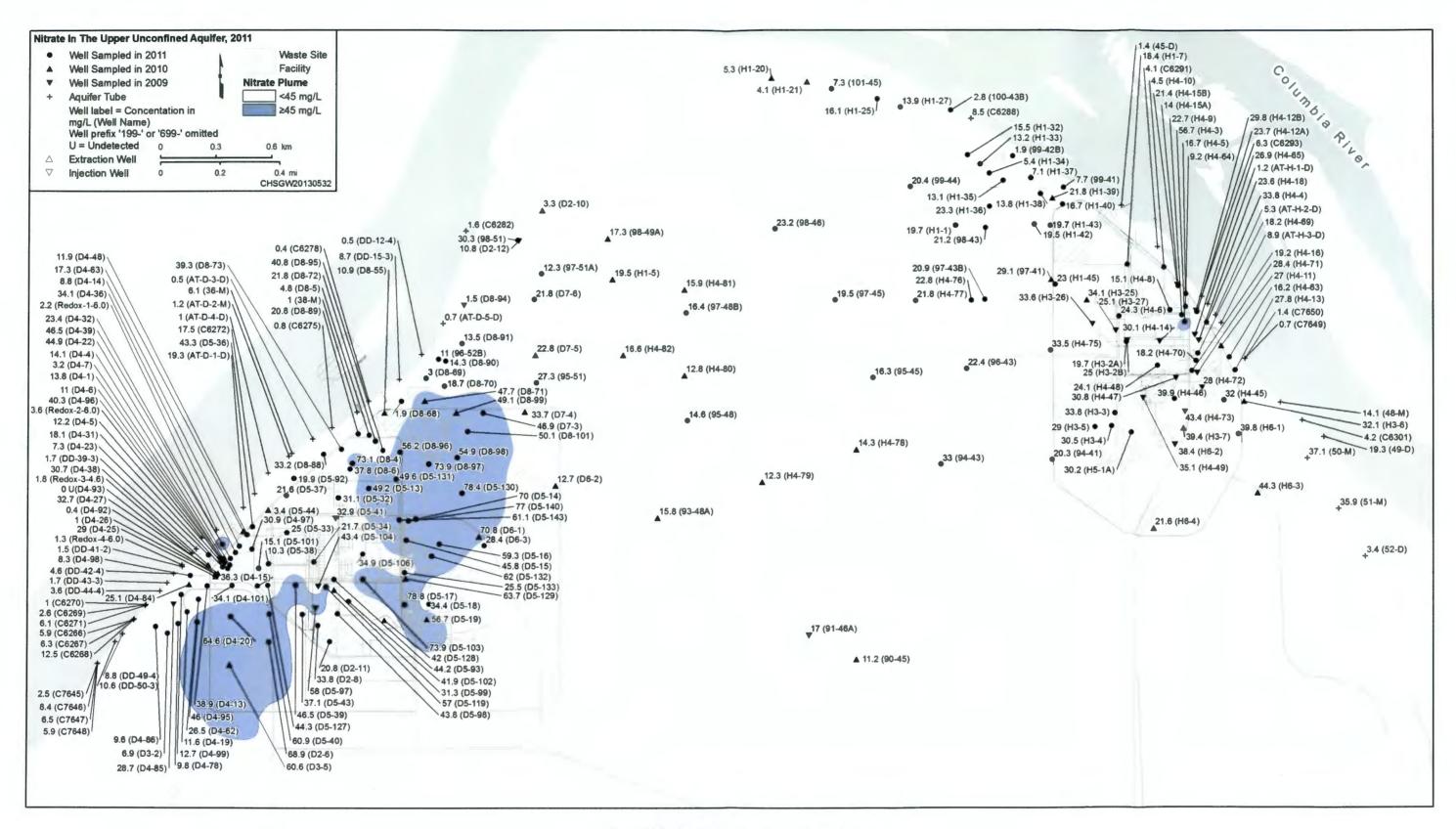
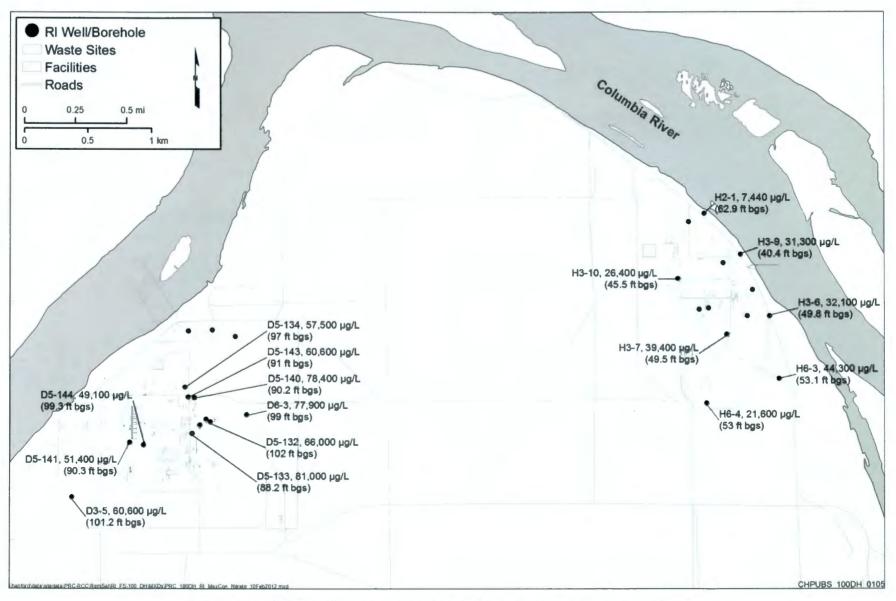


Figure 4-98. Nitrate Plume for 2011 at 100-D/H

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Figure 4-99. Maximum Nitrate Concentrations in Borehole Water Samples from RI Wells

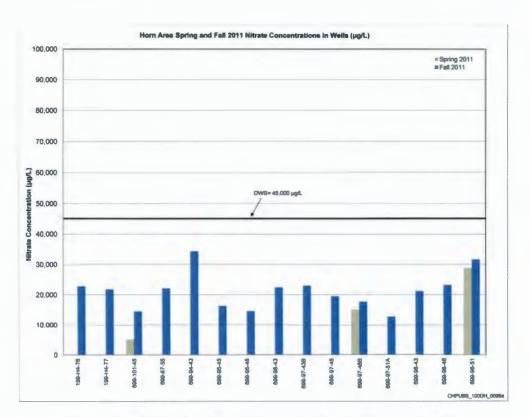


Figure 4-100. Horn Area Nitrate Concentrations in Monitoring Wells Spring and Fall 2011

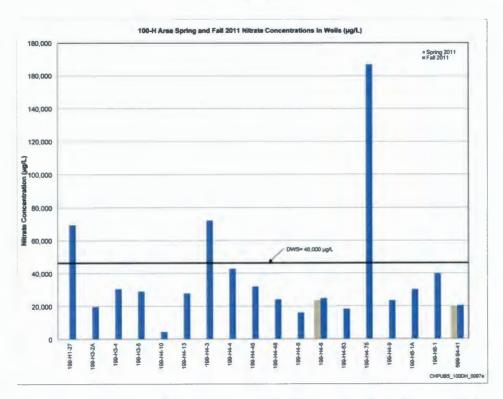


Figure 4-101. 100-H Area Nitrate Concentrations in Monitoring Wells Spring and Fall 2011

Table 4-23. Nitrate Sample Results from RI Drilling – 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Nitrate (µg/L)
	199-D3-5 (C7620, Well 2)	27.5 to 28.1 (90.3 to 92.3)	39,200 (D)
_		27.7 to 28.1 (90.9 to 92.3)	der der
100-D, Southern Plume: Unconfined Aquifer		29.3 to 29.7 (96 to 97.4)	47,800 (D)
d Aq		30.8 (101.2)	59,300 (D)
fine		30.8 (101.2)	60,600 (D)
ncon		31.4 (103)	59,300 (D)
e: U	199-D5-144 (C8668, Well R5 redrill)	28.01 (91.90)	
lum		28.01 (91.90)	42,100 (D)
rn P		29.11 (95.51)	
uthe		29.11 (95.51)	41,600 (D)
), So		30.27 (99.31)	41,200 (D)
00-D		31.49 to 31.64 (103.3 to 103.8)	49,100 (D)
-		31.49 to 31.64 (103.3 to 103.8)	47,800 (D)
		32.61 (107)	47,400 (D, N)
ells	199-D5-141 (C7625, Well R5)	27.5 (90.3)	
W		27.5 (90.3)	51,400 (D)
RU		29.1 (95.5)	43,000 (D)
100-D, Southern Plume: RUM Wells		29.1 (95.5)	42,500 (D)
Plu		30.6 (100.5)	40,800 (D)
hern		32.5 (106.5)	29,400 (D)
Sout		34.1 (112)	28,400 (D)
-D, S		49.5 (162.5)	2,090 (D)
100		94.1 (308.8)	168 (U, D)
9	199-D5-133 (C7621, Well 3)	26.9 (88.2)	
ıfine		26.9 (88.2)	81,000 (D)
ncon		28.3 (92.7)	68,600 (D)
e: U		29.8 (97.8)	72,600(D)
lum		29.8 (97.8)	73,000 (D)
100-D, Northern Plume: Unconfined Aquifer		31.4 (103)	74,800 (D)
	199-D5-132 (C7622, Well 4)	27 (88.7)	
N.		27 - 28.1 (88.7 - 92.3)	62,900 (D)
100-D		29.4 (96.4)	64,600 (D)
		29.4 (96.4)	63,300 (D)

Table 4-23. Nitrate Sample Results from RI Drilling – 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Nitrate (µg/L)
		31.1 (102)	66,000 (D)
		32. (105)	65,500 (D)
	199-D6-3 (C7623, Well 5)	28.7 (94)	
		28.7 (94)	77,900 (D)
		30.2 (99)	77,900 (D)
fer		30.2 (99)	77,000 (D)
100-D, Northern Plume: Unconfined Aquifer		30.9 (101.5)	77,000 (D)
peu	199-D5-140 (C7866, Well 9)	27.5 (90.2)	78,400 (D)
onfi		27.5 - 27.8 (90.2 - 91.3)	40.00
Unc		28.7 (94.2)	75,700 (D)
me:		28.7 (94.2)	76,600 (D)
Plu		30.2 (99)	73,500 (D)
hern		31.5 (103.3)	74,400 (D)
Vort	199-D5-143 (C8375, Well 9 redrill)	27.7 (91)	60,600 (D)
-D, I		27.7 (91)	
100		29. (95)	58,900 (D)
die de la constante de la cons		29. (95)	57,500 (D)
		31.2 (102.5)	57,100 (D)
		31.7 (104)	54,900 (D)
	199-D8-101 (C7852,	21.9 (72)	66,400 (D)
1996	Waste Site 116-DR-1&2)	21.9 (72)	~~
	199-D5-142 (C7857, Waste Site 118-D-6)	26.5 - 27.4 (87.1 - 89.8)	
ne: eholes		26.5 - 27.4 (87.1 - 89.8)	
Bor	Borehole C7850 (Waste Site 116-DR-9)	21.5 (70.4)	
iifer		21.5 (70.4)	
Aqu	Borehole C7851 (Waste Site 116-D-7)	20.3 - 21 (66.7 - 69)	
ined ined		20.3 - 21 (66.7 - 69)	
100-D, Northern Plume: Unconfined Aquifer Boreholes	Borehole C7855	27.8 (91.2)	
	(Waste Site 116-D-1B)	27.8 (91.2)	

Table 4-23. Nitrate Sample Results from RI Drilling - 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Nitrate (µg/L)
Well	199-D5-134 (C7624, Well R4)	28 (92)	
M		28 (92)	56,700 (D)
RUM		29.6 (97)	57,500 (D)
100-D, Northern Plume:		29.6 (97)	56,700 (D)
		31.1 (102)	53.100 (D)
		32.7 (107.3)	54,000 (D)
		41.3 (135.5)	2,900 (D)
		46.9 (154)	2,310 (D)
		82 (268.9)	1,560 (D)

Notes: Bold values exceed the DWS of 45,000 µg/L

Shaded cells indicate the sample was collected from a water-bearing unit below the RUM surface

Nitrate concentrations in wells screened in the first water-bearing unit of the RUM (199-H3-2C, 199-H4-12C, and piezometer 199-H4-15CS) are below the DWS and exhibit stable trends. The piezometer nest consisting of 199-H4-15CP, 199-H4-15CQ, and 199-H4-15CR is screened in various lower Ringold Formation water-bearing units and the basalt aquifer. Groundwater samples from all three piezometers had nitrate concentrations less than 10,000 µg/L in 2011. Three RI wells were also screened in the first water-bearing unit of the RUM: Well 199-H2-1 (C7631, Well R3), Well 199-H3-9 (C7639, Well R1), and Well 199-H3-10 (C7640, Well R2). Nitrate concentrations from the RI wells were less than 10,000 µg/L in the RUM.

Of the 13 RI wells installed at 100-H, 9 were sampled for nitrate as required in the SAP. Groundwater samples from these 9 wells had nitrate concentration less than the 45,000  $\mu$ g/L DWS. The concentrations in the unconfined aquifer range from 5,710  $\mu$ g/L at Well 199-H2-1 to 44,300  $\mu$ g/L at Well 199-H6-3. Analytical results collected at discrete depth intervals during drilling are presented in Table 4-24. The two RI aquifer tubes at 100-H (C7649 and C7650), located between the 116-H-7 Retention Basins and the river, had nitrate detected in groundwater at concentrations less than 10,000  $\mu$ g/L. In summary, little nitrate remains in 100-H above the DWS, except in a few isolated wells.

<sup>&</sup>quot;D" flag indicates that analysis was conducted at a secondary dilution factor.

<sup>&</sup>quot;N" flag indicates that the spike sample recovery was outside of the control limits.

<sup>&</sup>quot;-" indicates analyte was not sampled for at that location.

Table 4-24. Nitrate Sample Results from RI Drilling – 100-H

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Nitrate (µg/L)
	199-H3-6 (C7626, Well 6)	15.2 (49.8)	32,100 (D)
		15.2 - 15.8 (49.8 - 51.8)	
		16.4 (53.9)	31,300 (D)
	199-H3-7 (C7627, Well 7)	15.1 (49.5)	
		15.1 (49.5)	39,400
		15.7 (51.6)	38,200
		15.7 (51.6)	38,300
Too-II: Unconined Aquiler	199-H6-3 (C7628, Well 10)	14.8 (48.5)	44,100
Aq		14.8 (48.5)	
		16.2 (53.1)	44,300
		16.2 (53.1)	43,800
		19.5 (64)	41,800
	199-H6-4 (C7629, Well 11)	13.9 (45.7)	
		13.9 (45.7)	20,100
		13.9 (45.7)	20,200
		14.6 (48)	20,400
		16.2 (53)	21,600
		18.4 (60.5)	21,300
	199-H1-7 (C7630, Well 12)	NS	18,400
		NS	
	199-H2-1 (C7631, Well R3)	9.2 (30.1)	
		9.2 (30.1)	5,930
		9.2 (30.1)	5,710
		10.64 (34.9) <sup>a</sup>	6,550
		19.2 (62.9)	7,440
		48.2 (158.3)	2,060
		54.7 (179.6)	2,230
	199-H3-9 (C7639, Well R1)	12.3 (40.4)	
		12.3 (40.4)	31,300
		13.8 (45.2)	22,700
		13.8 (45.2)	22,500
		14.2 (46.5)	14,700

Table 4-24. Nitrate Sample Results from RI Drilling – 100-H

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Nitrate (µg/L)
		20.8 (68.4)	5,580
		40.8 (134)	1,930
		53.9 (177)	3,000
	199-H3-10 (C7640, Well R2)	13.9 (45.5)	
		13.9 (45.5)	26,400
		15.2 (49.9)	25,000
		15.2 (49.9)	24,400
		16.1 (52.8)	23,900
		60.4 (198)	3,520
		68.2 (223.6)	1,850

Notes: Bold values exceed the DWS of 45,000 µg/L

Shaded cells indicate the sample was collected from a water-bearing unit within the RUM.

NS = not specified

### 4.5.4 Strontium-90

The total footprint of the strontium-90 plume area exceeding the DWS of 8 pCi/L is approximately 0.2 km² (0.09 mi²). Strontium-90 was produced as a fission product in reactor fuel during the plutonium production operations. Contamination of water by fission products occurred commonly in the reactor fuel storage basins; water was released from the fuel storage basins by unplanned releases (i.e., leaks and spills), as well as during planned releases (e.g., basin water overflow during reactor defueling operations). In addition, reactor cooling water became contaminated with fuel and fission product residues during reactor fuel failure incidents. During these incidents, the reactor cooling water was typically diverted from the normal discharge directly to the river to liquid disposal trenches for discharge of the contaminated cooling water directly to the vadose zone. Leaks from the cooling water retention basins, as well as the intentional discharges of contaminated cooling water to the disposal trenches, accounts for most of the observed strontium-90 contamination in the vadose zone and groundwater. Figure 4-102 presents the strontium-90 plume at 100-D/H in 2010, and has remained relatively unchanged since then

100-D. Contamination of soil and groundwater by strontium-90 at 100-D Area is apparently related to both planned and unplanned releases of fission product-contaminated wastewater to the environment. Overflow water from the fuel storage basins was routed to the 116-D-1A and 116-D-1B liquid waste trenches. Both of these trench areas exhibit full-thickness vadose zone contamination by strontium-90. Well 199-D5-12, located just south of 116-D-1A liquid waste trench, historically exhibited strontium-90 in groundwater well above the DWS (i.e., up to 52.6 pCi/L) until it was decommissioned in 2002 (Figure 4-102). Well 199-D5-132, installed during the RI immediately adjacent to 116-D-1A Trench, exhibits strontium-90 in groundwater at about 44 pCi/L (Figure 4-103). Strontium-90 contamination observed in both of these wells is consistent with historical releases of contaminated wastewater to the trenches. Strontium-90 has been consistently below the minimum detectable activity (MDA) in all

<sup>&</sup>quot;D" flag indicates that analysis was conducted at a secondary dilution factor.

<sup>&</sup>quot;-" indicates analyte was not sampled for at that location.

sampling events in nearby upgradient existing Well 199-D5-16. Well 199-D5-15, located 127 m (418 ft) downgradient of the 116-D-1A and 116-D-1B trenches, has exhibited variable Sr-90 concentrations in groundwater ranging from about 1 to 5 pCi/L since 1992, with the most recent samples exhibiting no detectable activity.

Other wells near 116-D-7 and 116-DR-9 Retention Basins and 116-DR-1&2 Trench have historically exhibited strontium-90 in groundwater. These retention basins and trench received the single-pass reactor cooling water discharges from both 105-D and 105-DR reactors. Chronic leakage from the retention basins, as well as the intentional discharge of radiologically contaminated cooling water to the trench, resulted in the observed residual Sr-90 in groundwater in this vicinity. Monitoring Well 199-D8-68, located on the northern end of 100-D, had several DWS exceedances up until 2005, with no exceedances since that time.

Strontium-90 has not been detected in Well 199-D8-54B, which is completed in the first water-bearing unit of the RUM. Concentration trends in aquifer tubes (DD-15-2, DD-15-3, DD-15-4, DD-17-2, and DD-17-3) are variable, but all strontium-90 concentrations are below the DWS.

Of the 13 RI wells installed at 100-D, nine were sampled for strontium-90 as required in the SAP. Six of the nine wells had groundwater samples with concentrations less than the 8 pCi/L DWS. Wells 199-D3-5 (C7620, Well 2) and 199-D5-I32 (C7622, Well 4) both had detections that exceeded the DWS. Well 199-D3-5 had a maximum activity of strontium-90 in the unconfined aquifer of 8.5 pCi/L, at a depth of 31.4 m (103 ft) bgs. An analytical result of 4.5 pCi/L was also reported in the same borehole at 30.8 m (101.2 ft) bgs, the sample interval but slightly shallower. However, the duplicate sample at that depth was below the MDA. In addition, the gross beta results do not correlate with either the 8.5 or 4.5 pCi/L results, and there were known laboratory issues with strontium-90 results during the analysis period, introducing uncertainty to those results.

Strontium-90 activity at Well 199-D5-132 (C7622, Well 4) had a maximum value of 65 pCi/L in a fine-grained interval at a depth of 29.6 m (96.4 ft) bgs. The aquifer matrix at that depth and the sample interval above it, which had a reported value of 45 pCi/L, had a higher percentage of silt than other sample intervals in that borehole. The higher silt percentage may have retarded movement of the strontium-90. Well 199-D5-132 was drilled just outside the footprint of the 116-D-1A Trench, indicating that 116-D-1A is the likely source of strontium-90 to groundwater. In addition, strontium-90 concentrations in the unconfined aquifer at Well 199-D5-132 (C7622, Well 4) are similar to the historical strontium-90 concentrations detected in Well 199-D5-12, which had concentrations of 30 pCi/L detected in 1999 before decommissioning. Results from soil borehole C7857 had also had low activities, with levels consistently below 2 pCi/g. However, the maximum value was encountered slightly deeper in borehole C7857. These factors indicate that the fuel storage basin is also a likely source of strontium-90 in groundwater in that area, but not conclusively.

Sr-90 was detected in only one of four samples of the hyporheic zone from the four RI aquifer tubes at 100-D (C7645, C7646, C7647, and C7648) located southwest of the ISRM barrier. Strontium-90 was detected in aquifer tube C7646 at 3.2 pCi/L. Table 4-25 presents analytical data for groundwater aquifer grab samples collected during drilling activities. Figure 4-104 shows maximum strontium-90 concentrations identified in the nine RI wells.

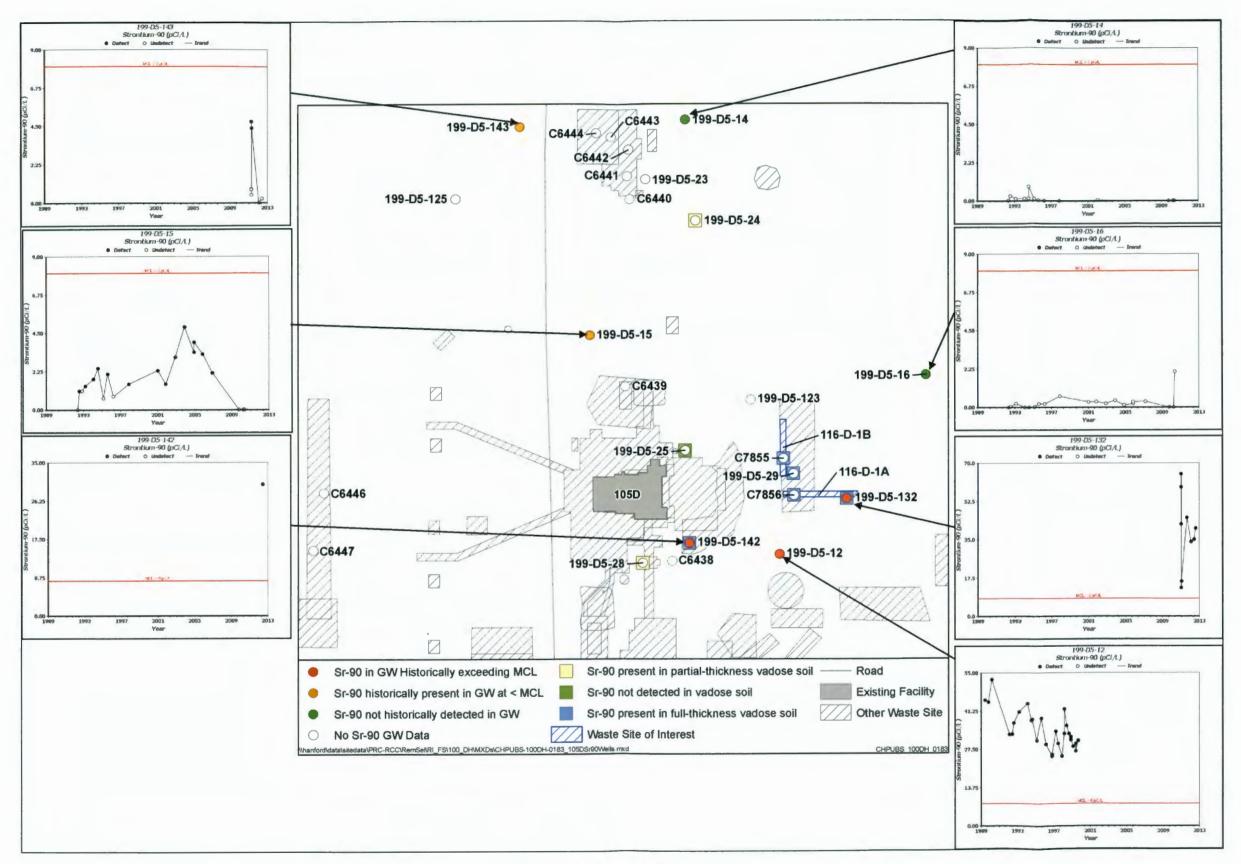


Figure 4-102. Strontium-90 at 100-D

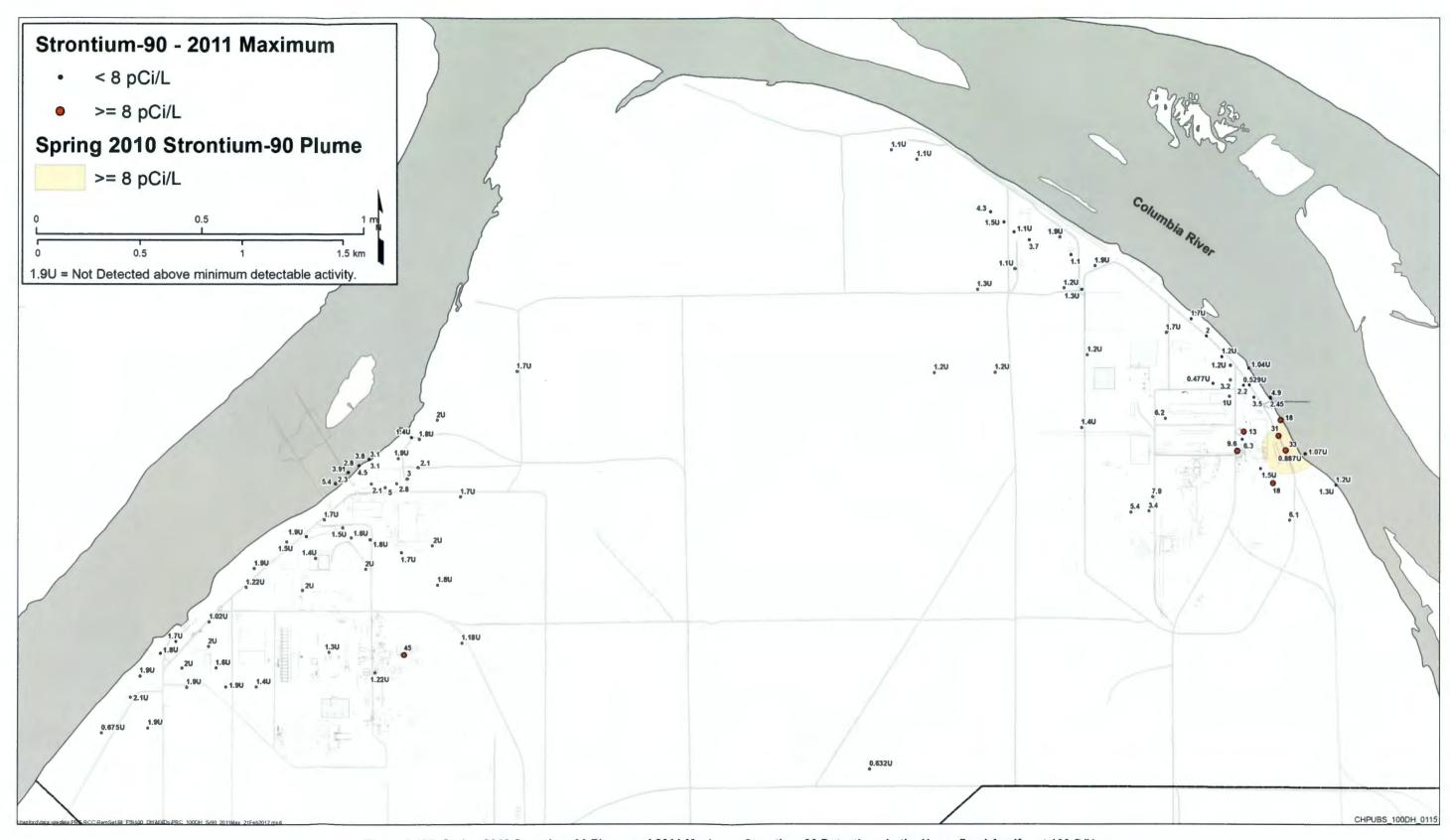


Figure 4-103. Spring 2010 Strontium-90 Plume and 2011 Maximum Strontium-90 Detections in the Unconfined Aquifer at 100-D/H

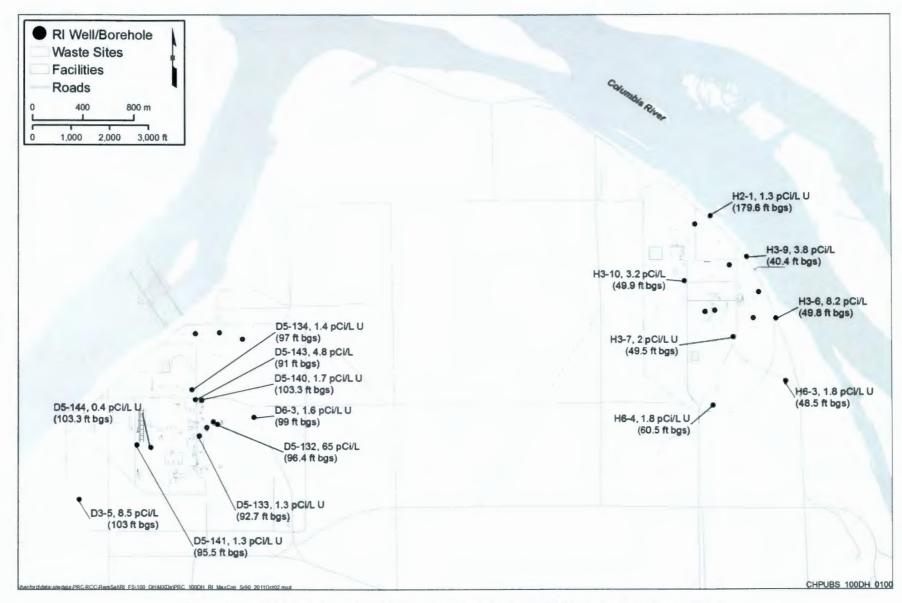


Figure 4-104. Maximum Strontium-90 Concentrations in Borehole Water Samples from RI Wells

Table 4-25. Strontium-90 Sample Results from RI Drilling – 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Strontium-90 (pCi/L)
	199-D3-5 (C7620, Well 2)	27.5 to 28.1 (90.3 to 92.3)	
		27.7 to 28.1 (90.9 to 92.3)	2 (U)
ifer		29.3 to 29.7 (96 to 97.4)	2.1 (U)
100-D, Southern Plume: Unconfined Aquifer		30.8 (101.2)	4.5
ined		30.8 (101.2)	2.1 (U)
conf		31.4 (103)	8.5
n C	199-D5-144	28.01 (91.90)	**
lum	(C8668, Well R5 redrill)	28.01 (91.90)	0.466 (U)
ern P		29.11 (95.51)	0.55 (U)
outh		29.11 (95.51)	0.575 (U)
D, S		30.27 (99.31)	0.519 (U)
100		31.49 to 31.64 (103.3 to 103.8)	
		31.49 to 31.64 (103.3 to 103.8)	0.438 (U)
		32.61 (107)	0.456 (U)
S	199-D5-141 (C7625, Well R5)	27.5 (90.3)	
Well		27.5 (90.3)	1.6 (U)
KUM		29.1 (95.5)	1.3 (U)
ne: F		29.1 (95.5)	1.5 (U)
Plur		30.6 (100.5)	1.4 (U)
100-D, Southern Plume: RUM Wells		32.5 (106.5)	1.7 (U)
Sout		34.1 (112)	1.6 (U)
0-D,		49.5 (162.5)	1.7 (U)
10		94.1 (308.8)	1.4 (U)
	199-D5-133 (C7621, Well 3)	26.9 (88.2)	
		26.9 (88.2)	1.3 (U)
		28.3 (92.7)	1.3 (U)
		29.8 (97.8)	1.6 (U)
		29.8 (97.8)	1.5 (U)
0		31.4 (103)	1.4 (U)
ined	199-D5-132 (C7622, Well 4)	27 (88.7)	
confifer		27 - 28.1 (88.7 - 92.3)	42
Plume: Unconfined Aquifer		29.4 (96.4)	65
Jume: Unconfine Aquifer		29.4 (96.4)	59

Table 4-25. Strontium-90 Sample Results from RI Drilling – 100-D

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Strontium-90 (pCi/L)
		31.1 (102)	13
		32. (105)	16
	199-D6-3 (C7623, Well 5)	28.7 (94)	
		28.7 (94)	1.8 (U)
		30.2 (99)	1.6 (U)
		30.2 (99)	1.7 (U)
		30.9 (101.5)	1.8 (U)
	199-D5-140 (C7866, Well 9)	27.5 (90.2)	
		27.5 - 27.8 (90.2 - 91.3)	1.7 (U)
		28.7 (94.2)	1.9 (U)
		28.7 (94.2)	1.8 (U)
		30.2 (99)	1.8 (U)
		31.5 (103.3)	1.7 (U)
	199-D5-143 (C8375, Well 9 redrill)	27.7 (91)	
		27.7 (91)	4.8
		29. (95)	1.6 (U)
		29. (95)	1.6 (U)
		31.2 (102.5)	1.6 (U)
		31.7 (104)	4.4
	199-D5-134 (C7624, Well R4)	28 (92)	
		28 (92)	1.7 (U)
		29.6 (97)	1.7 (U)
		29.6 (97)	1.4 (U)
ell		31.1 (102)	1.5 (U)
MM		32.7 (107.3)	1.5 (U)
100-D, Northern Plume: RUM Well		41.3 (135.5)	1.6 (U)
		46.9 (154)	2 (U)
PI		82 (268.9)	1.7 (U)

Notes: Bold values exceed the DWS of 8 pCi/L.

Shaded cells indicate samples collected from a water-bearing unit below the RUM surface.

<sup>&</sup>quot;U" flag indicates analyte was not detected above the minimum detectable activity (MDA) shown.

<sup>&</sup>quot;-" indicates analyte was not analyzed for at that location.

**100-H.** A plume of strontium-90 is present in the unconfined aquifer at 100-H, although the concentrations are at or less than the DWS over the majority of 100-H (Figure 4-102). Strontium-90 was likely released to the environment during historical reactor operations (i.e., to the vadose zone soil with subsequent migration to the underlying shallow unconfined aquifer) through planned and unintentional releases of contaminated water from the fuel storage basin and from releases of contaminated reactor cooling water to the 116-H-7 retention basin and the 116-H-1 Trench. Other waste sites that received radiologically contaminated liquids may also have contributed to the observed Sr-90 in soil and groundwater at 100-H. The Sr-90 plume has persisted because of the moderate to low mobility of strontium-90 in water, and its half-life of 28.79¹ years.

Strontium-90 concentrations observed in groundwater have generally declined over the past 20 years at 100-H; however, some locations continue to exhibit variable concentrations in excess of the 8 pCi/L. For example, extraction Well 199-H4-63, located midway between the 116-H-7 Retention Basin and the Columbia River, has exhibited a general downward concentration trend since 1996. Concentrations of Sr-90 in groundwater increased from 16 pCi/L to 31 pCi/L at this well during 2011 (inset Figure 4-105). The cause of this increase is not apparent and there may be several influences, including plume migration under the influence of the groundwater pump-and-treat system, seasonal transient effects of groundwater elevation, or the mobilization of strontium-90 under the effects of addition of water for dust control during remedial actions at nearby waste sites. Concentrations of strontium-90 in other nearby groundwater monitoring wells within the plume (e.g., 199-H4-11 and 199-H4-45) exhibit a similar trend, with general decreases in concentration since the early 1990s, and increases in the most recent year (inset Figure 4-105).

The possibility for strontium-90 concentrations to be affected by the pump-and-treat system operation became apparent in October 2009 when the pump-and-treat system was shut down for a Cr(VI) concentration rebound test at 100-H Area. Monitoring Wells 199-H3-2A, 199-H4-13, 199-H4-45, and extraction Well 199-H4-63 each exhibited a substantial increase in concentration in the period immediately following the system shutdown. Peak measured Sr-90 concentrations during these transients were 13 pCi/L, 23 pCi/L, 35 pCi/L, and 110 pCi/L in Wells 199-H3-2A, 199-H4-63, 199-H4-45, and 199-H4-13, respectively (see inset graphs in Figure 4-105).

Strontium-90 exhibits variable mobility in the vadose zone and aquifer system within the Hanford 100 Area. At 100-K, Sr-90 exhibits a moderate degree of mobility, such that high-concentration plumes have migrated away from the apparent release points, and transient concentrations approaching the MCL-equivalent of 8 pCi/L have been observed in aquifer tubes monitoring the Columbia River hyporheic zone. Similar conditions are apparent at 100-H, where Sr-90 concentrations exceeding the 8 pCi/L have been observed in nearshore wells and in samples collected from aquifer tubes completed in the hyporheic zone (e.g., Aquifer Tubes 47-D and 47-M, located at the river shore near Well 199-H4-11). Concentrations in the unconfined aquifer at 100-H exceeded the Sr-90 DWS of 8 pCi/L in five groundwater samples in fall 2011, and in three of the spring 2011 groundwater samples (Figure 4-106). The areal extent of the inferred strontium-90 plume varies seasonally; the concentration variation likely results from seasonal contact with contaminated vadose zone soil during periods of high river stage, which generally corresponds with higher groundwater elevations in the near-river portions of 100-H.

Strontium-90 concentrations in aquifer tubes are variable with some locations exceeding the DWS. Most aquifer tubes have concentrations below the reporting limit. The exceptions are aquifer tubes 47-D, 47-M, and C7649, which have concentrations fluctuating around the 8 pCi/L DWS.

<sup>&</sup>lt;sup>1</sup> Half-life from Radiochemistry Society website (RS, 2011) was accessed January 2012.

Figure 4-105. 100-H Fall and Spring Strontium-90 Plume in the Unconfined Aquifer

Of the RI wells installed at 100-H, seven were analyzed for strontium-90. Groundwater samples from six of seven wells had concentrations below the 8 pCi/L DWS. Strontium-90 was detected in Well 199-H3-6 at 8.2 pCi/L, slightly over the DWS. Figure 4-104 shows the maximum strontium-90 concentrations in the seven RI wells. Table 4-26 presents the strontium-90 results collected from discrete depth intervals during drilling. Results indicate a relatively localized area of strontium-90 that exceeds the DWS in the unconfined aquifer at 100-H, with no strontium-90 exceedances detected in lower water-bearing units in the Ringold Formation

Table 4-26. Strontium-90 Sample Results from RI Drilling - 100-H

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Strontium-90 (pCi/L)
	199-H3-6 (C7626, Well 6)	15.2 (49.8)	
		15.2 - 15.8 (49.8 - 51.8)	8.2
		16.4 (53.9)	5.9
-	199-H3-7 (C7627, Well 7)	15.1 (49.5)	
		15.1 (49.5)	2 (U)
		15.7 (51.6)	2.7 (U)
		15.7 (51.6)	2 (U)
uifer	199-H6-3 (C7628, Well 10)	14.8 (48.5)	
100-H: Unconfined Aquifer		14.8 (48.5)	1.8 (U)
ined		16.2 (53.1)	2.5 (U)
conf		16.2 (53.1)	2.6 (U)
. Un		19.5 (64)	1.8 (U)
Н-0	199-H6-4 (C7629, Well 11)	13.9 (45.7)	
10		13.9 (45.7)	2 (U)
		13.9 (45.7)	2 (U)
		14.6 (48)	2.2 (U)
		16.2 (53)	1.9 (U)
		18.4 (60.5)	1.8 (U)
	199-H1-7 (C7630, Well 12)	NS	
		NS	1.7 (U)
	199-H2-1 (C7631, Well R3)	9.2 (30.1)	
SI		9.2 (30.1)	1.7 (U)
We		9.2 (30.1)	2 (U)
100-H: RUM Wells		10.64 (34.9) <sup>a</sup>	1.9 (U)
H: 1		19.2 (62.9)	1.6 (U)
100-		48.2 (158.3)	1.4 (U)
		54.7 (179.6)	1.3 (U)

Table 4-26. Strontium-90 Sample Results from RI Drilling - 100-H

Area	Well Name (Borehole ID, SAP ID)	Sample Depth bgs m (ft)	Strontium-90 (pCi/L)
	199-H3-9 (C7639, Well R1)	12.3 (40.4)	
		12.3 (40.4)	3.8
		13.8 (45.2)	1.6 (U)
		13.8 (45.2)	1.4 (U)
		14.2 (46.5)	1.6 (U)
		20.8 (68.4)	1.8 (U)
		40.8 (134)	1.6 (U)
		53.9 (177)	1.7 (U)
	199-H3-10 (C7640, Well R2)	13.9 (45.5)	1.7 (U)
		13.9 (45.5)	3.2
		15.2 (49.9)	1.6 (U)
		15.2 (49.9)	1.8 (U)
		16.1 (52.8)	1.6 (U)
		60.4 (198)	1.7 (U)
		68.2 (223.6)	1.3 (U)

Notes: Bold values exceed the DWS of 8 pCi/L.

Shaded cells indicate samples collected from a water-bearing unit below the RUM surface.

NS = not specified.

<sup>&</sup>quot;U" flag indicates analyte was not detected above the MDA (minimum detectable activity) shown.

<sup>&</sup>quot;-" indicates analyte was not analyzed for at that location.

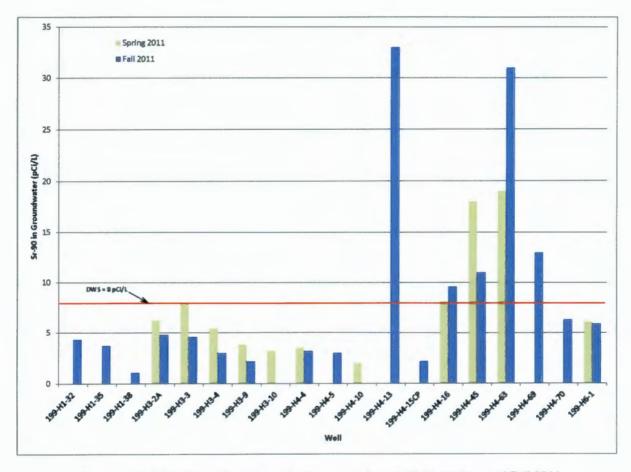


Figure 4-106. 100-H Area Strontium-90 Concentrations in Wells Spring and Fall 2011

## 4.5.5 Uranium

Uranium has been detected in groundwater monitoring wells located in 100-H downgradient of the 183-H Solar Evaporation Basins. In 1986, concentrations were as high as 2,090  $\mu$ g/L (Well 199-H4-3). The uranium concentrations in Well 199-H4-3 decreased as the basins were taken out of service, and then remediated in 1995. From 2006 through to 2011, concentrations in this well were consistently below the DWS. In surrounding wells concentrations also decreased over time, with some fluctuations that appear to be associated with water table changes. In October 2012, the concentrations in Well 199-H4-3 rose to 37.1  $\mu$ g/L, following historically high (near flood stage) river elevations in June of 2012, with the uranium levels dropping to 16.6  $\mu$ g/L when next sampled in February 2013.

Uranium was also detected above the DWS of 30  $\mu$ g/L in Well 199-H4-4 until 2002, and in Well 199-H4-12A until 2006. As shown in Figure 4-107, uranium concentrations in wells in that area have been declining over time. Well 199-H4-12A, which has concentrations that fluctuate at levels typically below the DWS, exhibits less of a trend, but overall also appears to be slowly declining.

Uranium concentrations in groundwater are likely attributable to the former use of the 183-H Solar Evaporation Basins, based on the nature of the waste that was treated at the site and the somewhat elevated activities in the upper interval of the pre-remediation boreholes. Concentrations in groundwater continue to fluctuate, apparently in response to water table changes.

Extraction in downgradient Wells 199-H4-4 and 199-H4-64 provides hydraulic control for contaminants in the area of the 183-H Solar Evaporation Basins.

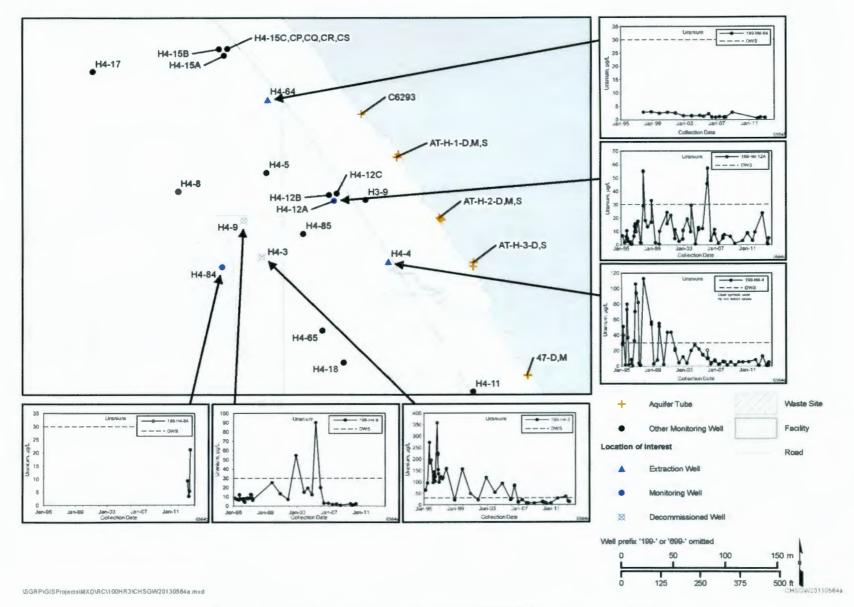


Figure 4-107. Uranium Concentrations near the 183-H Solar Evaporation Basins

# 4.5.6 Technetium-99

Technetium-99 (Tc-99) has been detected historically in wells downgradient of the solar evaporation basins at 100-H. The maximum value detected was 4,980 pCi/L in Well 199-H4-3 in 1995, during site remediation. In Well 199-H4-12A, a concentration of 1,312 pCi/L was detected in 1996. However, this value is suspect since the duplicate sample activity was reported as below the MDA at 0.22 pCi/L, a value that is consistent with the other reported values during that timeframe. Concentrations in Well 199-H4-12A have been consistently below 100 pCi/L since 2005.

Concentrations of Tc-99 are currently well below the DWS of 900 pCi/L, with the last exceedance being measured in Well 199-H4-3 in November of 1999 (1,070 pCi/L). The highest value since 1999 was a reported value of 870 pCi/L in 2006 (with a counting error of 170 pCi/L).

In Well 199-H4-3, levels rose slightly in 2012 to 120 pCi/L (October 2012). This level is well below the DWS of 900 pCi/L. The Tc-99 concentrations decreased considerably when the well was next sampled in February 2013, to 35 pCi/L.

#### 4.5.7 Tritium

Historically, tritium was detected in the unconfined aquifer at concentrations greater than the DWS of 20,000 pCi/L in several wells at 100-D. Tritium is not present in the Horn or 100-H above the DWS. By 1995, concentrations had decreased in most wells. Tritium concentrations in groundwater from Well 199-D5-17, located near 105-DR Reactor, displays typical trends for most wells (Figure 4-108) in 100-D. The primary sources of tritium are reactor operations at 105-D and 105-DR.

100-N has also contributed to the tritium now found in the unconfined aquifer underlying the southern portion of 100-D. As discussed in *Hanford Site Ground-Water Monitoring for 1993* (PNL-10082) a tritium plume was present at the 1325-N Crib (waste site 116-N-3). This plume later migrated to the northeast as shown in *Hanford Site Groundwater Monitoring for Fiscal Year 1997* (PNNL-11793, Plate 3). The remnants of this tritium plume are still identified by tritium concentrations in groundwater at or near 20,000 pCi/L in the southwestern portion of 100-D. Tritium has not been detected above the DWS of 20,000 pCi/L in wells/piezometers completed in the first water-bearing unit of the RUM. Figure 4-109 shows the tritium plume in the unconfined aquifer at 100-D/H in 2010, as well as the maximum values of tritium detected in 2011. Activities of tritium in the 2011 and 2012 groundwater samples were below the DWS of 20,000 pCi/L, with the exception of on reading in February 2011. A concentration of 24,000 pCi/L was detected in Well 199-D8-89; however, the duplicate sample result was 180 pCi/L and is consistent with the other results for that well. The results are considered suspect and are being reviewed.

In 2011, the maximum tritium concentration in the unconfined aquifer underlying 100-D was identified in Well 199-D8-89 at 24,000 pCi/L, from February 2011. This also represented the only location with concentrations over 20,000 pCi/L. The duplicate sample was reported at 180 pCi/L, which is more consistent with historical concentrations in that area, and consistent with subsequent sample results. The February 2011 result was evaluated by the laboratory, which indicated the sample was biased high and other quality control errors were present. As a result, along with the presence of a duplicate sample result, the data was rejected.

Of the 25 RI wells installed throughout 100-D/H, 15 were sampled for tritium. Tritium was identified in groundwater samples during drilling in Wells 199-D5-132 and 199-D5-133 at 11,000 and 10,000 pCi/L, respectively. Elevated concentrations in this location are associated with the fuel storage basin and Fuel Storage Basin Trench (100-DR-1). Figure 4-110 shows that the maximum concentration in groundwater sample from Well 199-D6-3 was 20,000 pCi/L, which is equal to the DWS. This well also had the highest reliable tritium concentration detected at 100-D/H. Tritium contamination identified in the unconfined

aquifer at Well 199-D6-3 may be associated with the upgradient 118-D-4 Burial Grounds, which had known reactor components and tritium. Soil samples collected from the borehole for Well 199-D6-3 did not have tritium detected, which provides further evidence of an upgradient source. Results from 2011 groundwater sampling were an order of magnitude lower, at 2,600 pCi/L. This introduces uncertainty regarding the actual tritium concentrations at that location.

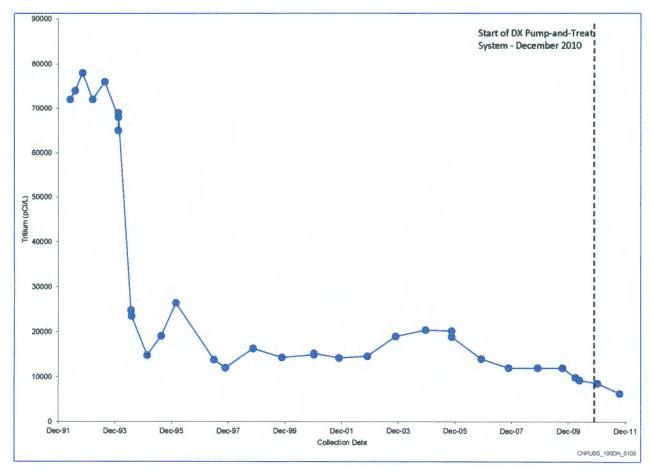


Figure 4-108. Tritium Concentrations in Groundwater over Time in Well 199-D5-17

Groundwater samples collected during drilling of RI Well 199-D3-5 had a maximum tritium concentration of 17,000 pCi/L. This well is located downgradient of the 118-D-2:1 Burial Ground, which has both tritium and strontium-90 identified among the potential COPCs.

# 4.5.8 Zinc

Historically, elevated concentrations of zinc in the unconfined aquifer have been found beneath 100-D. Zinc has been detected in the unconfined aquifer and the first water-bearing unit of the RUM. Detections in both aquifer units have been sporadic in most locations and do not have a consistent trend. The maximum concentration (from 2007 to 2011) identified in an aquifer tube was at Redox-4-6.0, which is located downgradient of the ISRM barrier. The concentration of 119  $\mu$ g/L is at the high end of background concentrations at Hanford.

Sources of zinc contribution to groundwater have not been isolated, but possibilities include trace amounts of zinc in iron oxide that was liberated during reduction associated with the ISRM, and/or trace zinc that may have been present in the sodium dithionite if it was manufactured using the zinc process.

However, because zinc exceedances are present in the unconfined aquifer in other areas of 100-D/H, the ISRM barrier could not have been the only source.

Another possible source is from mobilization of zinc from the soil under acidic conditions, which did occur during reactor operations. As presented in *Solubility and Mobility of Copper, Zinc and Lead in Acidic Environments* (Reddy et al., 1995), the availability and mobility of zinc will increase in low pH environments.

Concentrations in groundwater samples from wells correlating with the 100-D southern Cr(VI) plume (199-D5-17, 199-D5-18, and 199-D5-40) have exceeded 91  $\mu$ g/L, the standard for zinc where water is discharged to surface water. Groundwater samples in 100-H have also had zinc concentrations above the 91  $\mu$ g/L level. The elevated concentrations are not consistent, and do not have a trend. In the first water-bearing unit of the RUM underlying 100-D (199-D8-54B), zinc was identified at concentrations just below 91  $\mu$ g/L. Zinc has also been detected in wells completed in the RUM in the Horn, and in 100-H, at concentrations ranging from at or near the detection limits to as high as 89  $\mu$ g/L on one occasion. In 100-H, zinc concentrations in groundwater from Well 199-H4-2, which is screened in the basalt, have been well below the water quality standard consistently since late 1994. In these lower aquifers, as with the unconfined aquifer, there is no apparent trend or consistent detection.

During drilling activities for RI wells, water samples were collected at discrete depth intervals and analyzed for zinc. The resulting maximum zinc concentrations in the unconfined aquifer underlying 100-D ranged from 17 to 331  $\mu$ g/L, and at 100-H unconfined aquifer concentrations ranged from 12 to 291  $\mu$ g/L. No apparent distribution trends were observed.

#### 4.5.9 Carbon Tetrachloride

Carbon tetrachloride is present in the unconfined aquifer in limited amounts underlying 100-D/H. A source has not been identified, although it could be associated with liquid waste site discharges.

The distribution of carbon tetrachloride in 100-D/H groundwater in fall 2009 is shown on. The detection limit (1  $\mu$ g/L) exceeds the 0.23  $\mu$ g/L (Clean Water Act – Human Health Water + Organism), so only exceedances of the detection limit are highlighted on the base map. Concentrations in the unconfined aquifer from monitoring wells at 100-D, 100-H, and the Horn all show decreasing trends and most recent concentrations are below the detection limit. In 100-D/H, groundwater from the first water-bearing unit of the RUM has had a limited number of sampling events.

Based on the carbon tetrachloride groundwater sampling data collected from the RI wells, only one sample had carbon tetrachloride detected above the detection limit. Well 199-H3-9 (C7639, Well R1), at a depth of 40.8 m (134 ft) bgs, had a detected value of 2.7  $\mu$ g/L. The sample is "J" flagged, meaning the sample was detected above the MDL but less than the practicable quantitation limit. All groundwater samples from aquifer tubes were below the detection limit of I  $\mu$ g/L.

## 4.5.10 Chloroform

Chloroform is a minor contaminant present in the unconfined aquifer in limited amounts at 100-D/H. A source has not been identified, though it could be associated with liquid waste site discharges or the biodegradation of carbon tetrachloride.

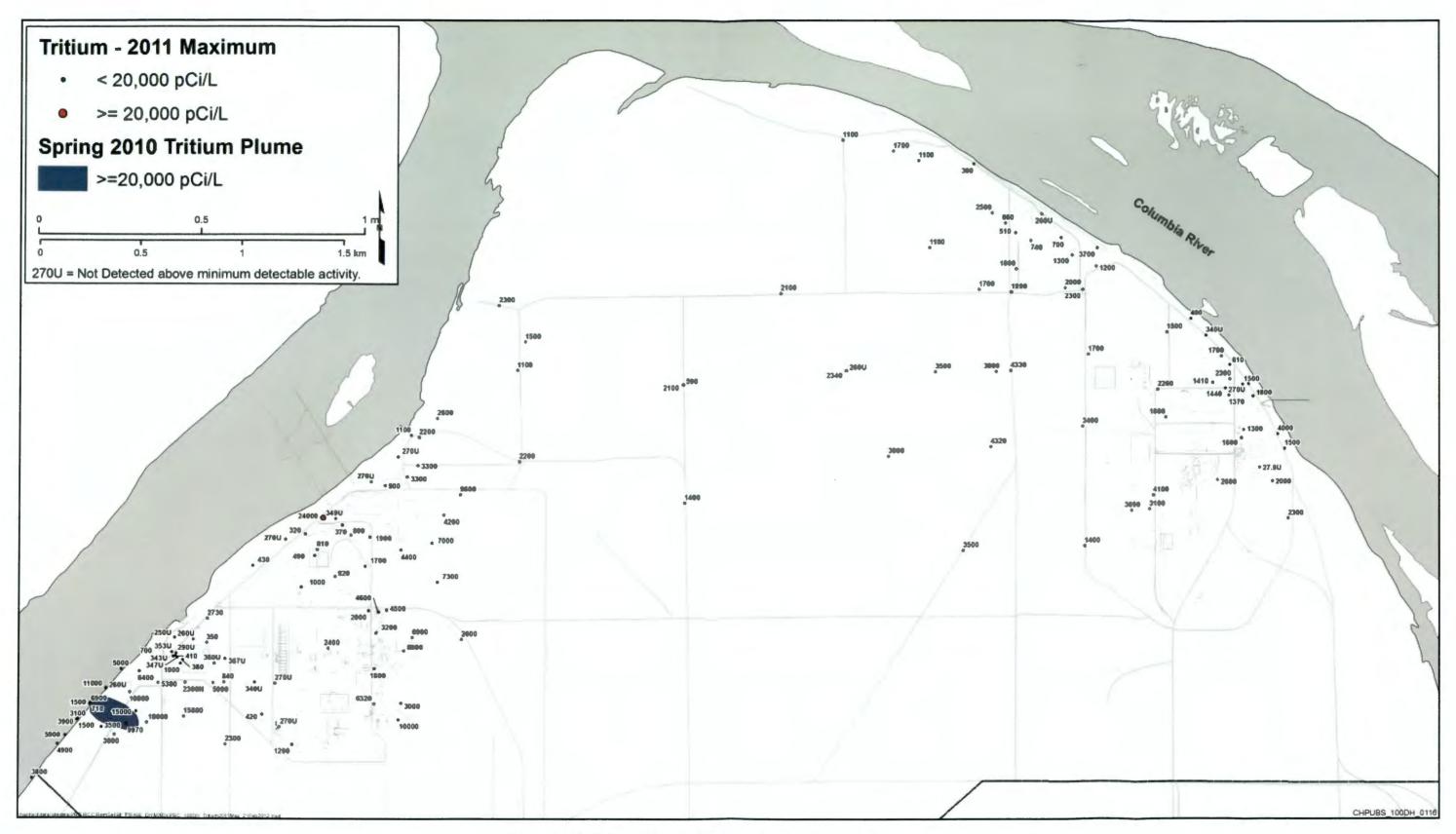


Figure 4-109. Spring 2010 Tritium Plume and Maximum 2011 Concentrations

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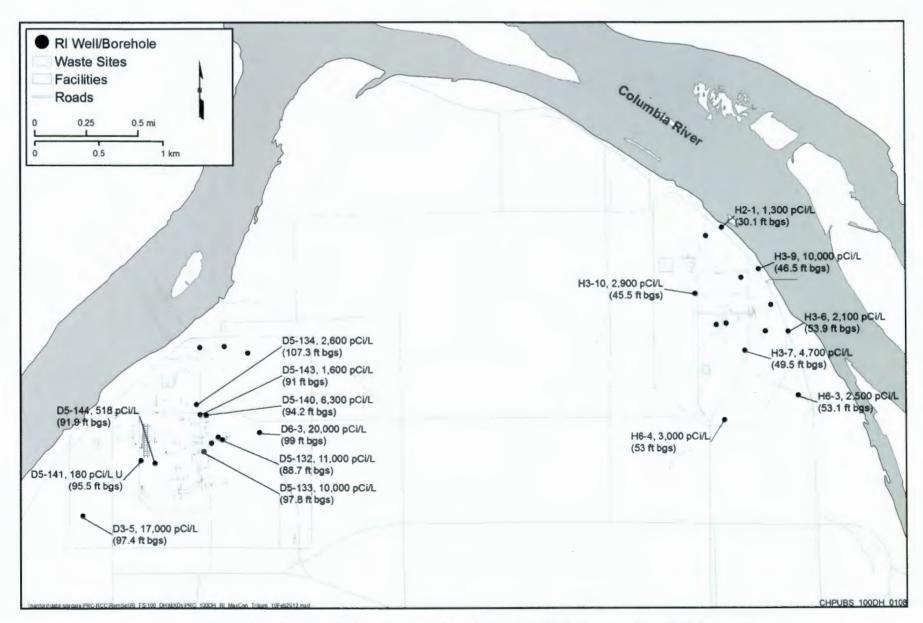


Figure 4-110. Maximum Tritium Concentrations in Borehole Water Samples from RI Wells

Chloroform has been sporadically detected in the unconfined aquifer underlying 100-D/H, with concentrations ranging from below detection to 53  $\mu$ g/L (Well 199-H4-47 in 1992). Since 1998, chloroform has not been detected in groundwater underlying 100-D/H above 10  $\mu$ g/L. Except for chloroform detected in Well 199-H4-5, chloroform concentrations are not associated with a specific location or with a trend.

The highest concentration detected was from Well 199-D5-143 (3.4  $\mu$ g/L). Chloroform concentrations in groundwater samples from the RI aquifer tubes were below action levels. Groundwater samples from the first water-bearing unit of the RUM have not been analyzed for chloroform.

#### 4.5.11 Sulfate

Sulfate is present in the unconfined aquifer underlying a large portion of 100-D but with only occasional detections at 100-H. Sulfate in the unconfined aquifer at 100-D, not associated with the ISRM barrier, is a result of sulfuric acid being used primarily as a decontamination solution with some used in water treatment. In addition, mercury-contaminated, commercial-grade sulfuric acid was used for cooling water pH adjustment at 100-K (1968 to 1977). Although this period was after the shutdown of the 100-D/H reactors, mercury contamination associated with sulfuric acid has been identified during the remediation of the 100-D-77 waste site at the 183-DR Head House.

Before 2005, sulfate concentrations in the unconfined aquifer underlying the southern area of 100-D exceeded 1,000,000  $\mu$ g/L. These high concentrations were associated with injections of sodium dithionite solution at the ISRM barrier, which elevated sulfate concentrations in groundwater along the barrier and in some downgradient wells and aquifer tubes. However, since 2005, concentrations have dropped to less than 500,000  $\mu$ g/L. The secondary DWS for sulfate is 250,000  $\mu$ g/L.

A portion of the 183-H Solar Evaporation Sedimentation Basins was used as an evaporation treatment facility for neutralized acid wastes. Four of the basins were converted for use as solar evaporators after cessation of reactor operations at 100-H. The neutralized nitric and sulfuric acid wastes, generated by reactor fuel fabrication processes in the 300 Area were transferred to the open-topped basins and allowed to evaporate. The basins apparently leaked substantial amounts of waste to the vadose zone, creating a high-concentration groundwater plume of nitrate, sulfate, mercury, and other metals.

Sulfate has been analyzed for in groundwater samples from wells/piezometers in the first water-bearing unit of the RUM as well as in the RLM unit in the recent 5-year period, with no exceedances of  $250,000 \mu g/L$  (DWS).

#### 4.5.12 Other Contaminants Evaluated in the RI

As presented in the 100-D/H SAP (DOE/RL-2009-40), groundwater COPCs and several additional analytes were identified for evaluation during the RI. In addition to the statistical evaluation of historical data presented in Section 4.2.1, the analytical data from the RI groundwater monitoring wells were also evaluated. The following contaminants that were detected in borehole groundwater samples from RI wells, yet not discussed separately, are shown in Table 4-27.

**Radionuclides.** Groundwater analysis conducted during the RI resulted in the detection of two radionuclides, other than those discussed separately: europium-154 and technetium-99. The remaining radionuclides that were analyzed per the 100-D/H SAP (DOE/RL-2009-40) were not detected above the MDA.

Europium-154 was detected in a groundwater sample from Well 199-D3-5 (C7620, Well 2) at 57 pCi/L. However, the total analytical error reported by the laboratory was 71 pCi/L, making this result questionable.

Table 4-27. Other Contaminants Evaluated in the RI and Detected

Radionuclides	Metals, Ions,	and Anions	Volatile Organic Carbon
Technetium-99	Aluminum	Phosphorus	Acetone
Europium-154	Barium	Potassium	Tetrachloroethene
Gross alpha Gross beta	Boron	Selenium	Toluene
	Calcium	Silicon	
	Cobalt	Sodium	
	Copper	Uranium	
	Iron	Vanadium	
	Lead		
	Magnesium		
	Manganese		
	Molybdenum		
	Nickel		

Technetium-99 was detected in groundwater samples collected from several RI wells, as presented in Table 4-28.

Table 4-28. Detections of Technetium-99 in RI Wells - Borehole Groundwater Samples

Well Name	Boring ID	SAP ID	Result (pCi/L)
199-D3-5	C7620	Well 2	190
199-Н6-4	C7629	Well 6	68
199-H2-1	C7631	Well R3	100
199-Н3-9	C7639	Well R1	18
199-H3-10	C7640	Well R2	10

Values for gross alpha ranged from below the MDA to 14 pCi/L in Well 199-H3-10 (C7640, Well R2), with all but two detections below 10 pCi/L. Gross beta values ranged from below the MDA to 130 pCi/L in Well 199-D5-132 (C7622, Well 4). With the exception of the detections in that one location (Well 199-D5-132), the remaining gross beta results were below 22 pCi/L, with most detections below 10 pCi/L.

**Metals, lons and Anions.** Several metals were evaluated in groundwater as shown in Table 4-27. The maximum detections are presented in Table 4-29.

Volatile Organic Compounds. Groundwater samples collected from RI wells during drilling had the following VOCs detected: acetone had a maximum detection of 4.9  $\mu$ g/L, tetrachloroethene had a maximum detection of 2.8  $\mu$ g/L, and toluene had a single detection of 1.3  $\mu$ g/L. No other VOCs were detected.

Table 4-29. Maximum Detections of Metals, Ions and Anions in RI Wells –
Borehole Groundwater Samples

Analyte	Maximum Concentration (μg/L)	Analyte	Maximum Concentration (μg/L)
Aluminum	3,320	Molybdenum	36.8
Barium	471	Nickel	20.3
Boron	96.2	Phosphorus	55.7 (one detection)
Calcium	118,000	Potassium	7,420
Cobalt	8.12	Selenium	5.36 (one detection)
Copper	136	Silicon	20,800
Iron	1600	Uranium	6.75
Lead	8.36	Vanadium	37.3
Magnesium	32,900		
Manganese	777		

## 4.5.13 Secondary Groundwater Effects of the ISRM and In-Situ Treatability Testing

The implementation of the ISRM treatability test, the full-scale ISRM barrier, the micron-scale ZVI treatability test, and the three biostimulation treatability tests, have produced localized reducing zones in the 100-D Area and, to a lesser extent, in the 100-H Area, that had the ability to reduce the concentrations of Cr(VI) in groundwater. The locations of the various tests are presented in Section 1.2.3.5, Treatability Studies, and shown in Figure 1-30. The effective longevity of the ISRM treatment zone capacity was originally estimated at 23 years (100-D Area In Situ Redox Treatability Test for Chromate-Contaminated Groundwater [PNNL-13349]). The ZVI treatability test was conducted within a section of the ISRM treatment zone. Consequently, the longevity of the reducing conditions in the area amended by the injection of ZVI is uncertain, but should exceed 23 years. Given the smaller scale of the three biostimulation treatability tests (relative to the installation of the ISRM barrier), oxidizing conditions are expected to be more rapidly re-established in the aquifer at the biostimulation test areas.

As a result of the implementation of the treatability tests and the full-scale ISRM system, the concentrations of some groundwater constituents (hereafter referred to as secondary contaminants) to elevated levels relative to their background concentrations for groundwater. Many of these secondary contaminants are redox-sensitive metals (e.g., iron, manganese, arsenic) that have mobilized from the reducing zones that were established by ISRM and the treatability tests. The secondary contaminants that are of primary concern are discussed in the following sections.

Sulfate Sulfide, Bromide, and Nitrite. The ISRM was created by the injection of the inorganic reducing agent sodium dithionite  $(Na_2S_2O_4)$ . The in situ redox conditions established by the sulfite  $(S^{3^+})$  in sodium dithionite are above the stability field for sulfide but are sufficiently reducing to reduce oxidizing dissolved constituents (e.g., nitrate, DO) in groundwater reductively dissolve ferric hydroxides and manganese oxides in the aquifer matrix and to reductively dissolve iron and manganese hydroxides and oxides in the aquifer matrix. During these oxidation-reduction reactions, the sulfite in sodium dithionite is oxidized to sulfate. This process has produced the elevated concentrations (relative to background) of sulfate observed in the vicinity of, and down-gradient of, the ISRM. Owing to the mobility of sulfate, moderately elevated concentrations of sulfate will likely be maintained in the vicinity and down-gradient of the ISRM until the sulfite in the injected sodium dithionite has been fully oxidized to sulfate. Unlike the ISRM, neither the ZVI nor the biostimulation treatability tests resulted in notable local increases in the

concentrations of sulfate in the aquifer. Conversely, some naturally occurring sulfate was likely reduced to sulfide within the reducing zones produced by these treatability tests. The resulting concentrations of sulfide in groundwater would have been kept very low by the precipitation of ferrous iron monosulfide (FeS), a very low solubility phase.

Bromide concentrations above background levels have been detected in the vicinity of one or more of these treatability test areas. These levels reflect the use of bromide salts as a groundwater flow tracer during treatability testing. Owing to the limited duration of these treatability tests, any bromide concentrations dissipated within a few years of test completion.

Nitrite detections have been reported in the 100-HR-3 OU groundwater. Although nitrite is naturally produced during the denitrification of nitrate, this process typically does not occur in oxygenated aquifers such as the Hanford formation. The low DO conditions locally established by the ISRM and the biostimulation treatability tests have likely facilitated the production of the observed low levels of nitrite at the area. Nitrite is highly susceptible to additional reduction processes and is not typically a long-lived species in reducing groundwater. The production of additional low levels of nitrite is expected to cease once oxidizing conditions are re-established in the treatment zones.

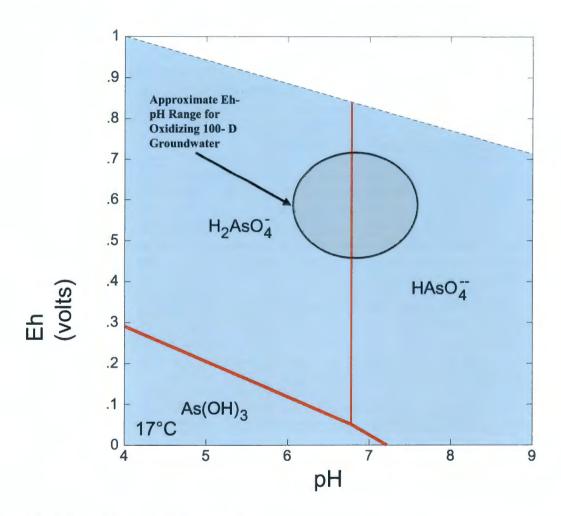
Iron and Manganese. Although not implemented as full-scale treatments, the 100-D in situ treatability tests conducted using micron-scale ZVI, molasses, and vegetable oil and the polylactate treatability test conducted at 100-H, have produced detectable concentrations of many of the same secondary contaminants produced by the ISRM. The ISRM, associated ZVI testing, and the biostimulation treatability tests established reducing conditions in the naturally oxidizing Hanford formation that were sufficient to locally solubilize iron and manganese hydroxides and oxides and associated trace constituents such as arsenic, selenium, thallium, and zinc.

Once oxygen and nitrate have been depleted in groundwater by sodium dithionite, ZVI, or microbial activity, Mn (IV) oxides, iron (Fe[III]) hydroxides in the matrix of the formerly oxidizing aquifer, are subject to reductive dissolution processes. Ferric iron and Mn (IV) are rapidly reduced by sulfide that is produced by microbially-mediated sulfate reduction, and sulfate reduction is commonly associated with the implementation of in situ biostimulation and ZVI barriers.

The reductive dissolution of manganese and iron oxides at the ISRM and testing sites has locally introduced elevated levels (relative to background) of relatively mobile Fe (II) and Mn (II) species into the groundwater. This Fe (II) and Mn(II) will largely remain in the soluble divalent state until it is transported to the periphery of the reducing zone (where dissolved oxygen has not been depleted), where these metals will be re-oxidized and re-precipitated as hydroxides and oxides. Divalent iron and manganese may continue to be solubilized within the ISRM treatment zone and the smaller biostimulation test zones, until more oxidizing groundwater conditions are re-established.

Trace Metals Solubilized by Reductive Dissolution of Iron and Manganese Oxides and Hydroxides. Iron and manganese oxides present in aquifer materials commonly contain trace metals (e.g., arsenic, thallium, mercury, cadmium, lead, zinc and copper) at concentrations that are notably higher than the concentrations in the bulk matrix. These metals are concentrated in the iron and manganese oxides and hydroxides due to sorption and co-precipitation processes that occur naturally over time in aquifers. Not uncommonly, reductive dissolution of oxidized iron and manganese phases during biostimulation (and other reduction-based treatments), also solubilizes these trace elements. Once mobilized from the aquifer matrix, these trace metals may remain in solution at concentrations above the pre-treatment background levels in those areas where reducing conditions persist.

Arsenic. Dissolved arsenic (As) may be an environmental concern, even when present in groundwater at relatively low concentrations (MCL of 0.01 mg/L). Arsenic in groundwater is commonly found in either the trivalent (III) or the pentavalent (V) state. Both As III and As V form stable hydroxyl complexes in groundwater and the pH is the most important factor that controls the dominant hydroxyl complex that is stable. A Pourbaix diagram illustrating the equilibrium-based speciation of As V and As III over a range of Eh-pH conditions is presented in Figure 4-111. The oval-shaped area shown in this plot illustrates that As V species should predominate under the range of natural groundwater Eh and pH conditions within the Hanford Formation (i.e., not impacted by the ISRM or by biostimulation testing).



Note: (25 C and 1.0 Atm, Arsenic = 0.015 mg/L)

Figure 4-111. Arsenic Speciation as a Function of pH and Oxidizing to Moderately Reducing Eh Conditions

The hydroxyl complexes of As III or As V that predominate under circum-neutral pH and oxidizing groundwater conditions (typical of the Hanford Formation at 100-HR-3), are strongly sorbed by FHO's in the aquifer matrix ("Arsenite and Arsenate Adsorption on Ferrihydrite: Kinetics, Equilibrium, and Adsorption Envelopes" [Raven et al., 1998]). However, iron oxy-hydroxides have been solubilized in those parts of the Hanford Formation where strongly reducing conditions have been temporarily established by the implementation of the ISRM or by biostimulation testing. The reductive dissolution of these iron oxy-hydroxides has resulted in the mobilization of the arsenic that had been previously adsorbed. Once solubilized, this arsenic will form As III and /or AsV hydroxyl species that will remain

relatively mobile until transported outside the locally reducing area produced by the ISRM or the biostimulation tests. Owing to the high affinity of As III and As V species for FHOs, arsenic concentrations should return to non-detectable levels in the aquifer, once oxidizing conditions are reestablished (even in those currently strongly reducing areas directly affected by the ISRM or the biostimulation tests).

Lead. Dissolved Pb forms relatively weak aqueous complexes with most common inorganic anions (e.g., carbonate nitrate, chloride, and sulfate). The neutral species PbSO4 is moderately stable, and the concentrations of this species can constitute a significant fraction of the soluble Pb species in aqueous solutions containing elevated concentrations (relative to background) of sulfate (e.g., 100 mg per liter) (Chemical Equilibria in Soils [Lindsay, 1979]). In general, the dissolved Pb in soil pore water with a pH of 9 or below, will exist predominantly as the cationic Pb2+ and PbOH+ species (Chemical Equilibria in Soils [Lindsay, 1979]; 1997; Use of Apatite for Chemical Stabilization of Subsurface Contaminants Final Report [Bostick et al., 2003]). Depending on the soil pH and the relative abundance of dissolved organic compounds, the solubility and mobility of Pb in soils can be increased by the formation of organo-Pb complexes (Issue Paper on the Environmental Chemistry of Metals [Langmuir et al., 2004]). In the absence of dissolved organic ligands, the inability of Pb to form strong aqueous complexes with most inorganic species will result in the probable sequestration of much of the Pb in circum-neutral pH soils by sorption onto clay minerals, the oxides and oxy-hydroxides of iron and manganese, and particulate organic matter, and by mineral precipitation reactions (Use of Apatite for Chemical Stabilization of Subsurface Contaminants Final Report [Bostick et al., 2003]). Lead minerals that are known to precipitate in Pb-contaminated soils range from those that are variably soluble at acidic to circum-neutral pH (PbSO4 [anglesite], PbCO3 [cerussite], and PbO [litharge]).

If iron-reducing conditions develop in Pb-contaminated soils (for example, in the biostimulation treatability zones), Pb concentrations in solution may increase as iron oxy-hydroxides undergo reductive dissolution and sorbed Pb is released into solution ("Solubility of Heavy Metals in a Contaminated Soil: Effects of Redox Potential and pH" [Chuan et al., 1996]). If sulfate- reducing conditions are established, however, Pb concentrations should be reduced to very low concentrations by the formation of low-solubility Pb sulfide phases (*Use of Apatite for Chemical Stabilization of Subsurface Contaminants Final Report* [Bostick et al., 2003]). Once dissolved lead is transported out of the reducing zone, or oxidizing conditions are re-established, this heavy metal will be readily readsorbed by iron oxy-hydroxides.

**Cadmium.** In most geologic systems, Cd is stable in the 2+ valence state. Primary Cd minerals are not abundant in nature. The aqueous Cd2+ ion is stable over a large range of Eh and pH conditions, and it is the predominant species in most dilute aqueous systems with a circum-neutral to acidic pH. As the pH of dilute, carbonate poor, aqueous solutions approached a value of about 8, hydrated species of Cd (e.g., CdOH<sup>+</sup>) become increasing important (*Chemical Equilibria in Soils* [Lindsay, 1979]). In general, the common anions chloride, nitrate, phosphate and, to a lesser extent, sulfate do not complex significantly with Cd in soil pore water solutions unless these ions are present at relatively high concentrations (*Chemical Equilibria in Soils* [Lindsay, 1979]). However, at a pH above about 7 and in the presence of carbonate, cadmium may precipitate as the low solubility phase otavite (CdCO<sub>3</sub>). Nevertheless, in oxidizing groundwater systems with a circum-neutral pH, cadmium solubility is commonly limited by sorption to aquifer phases such as clay minerals, organic material, manganese oxides and, in particular, iron oxy-hydroxides. As described above for lead, any detectable levels of cadmium mobilized within the ISRM or treatability test reducing zones will be subject to re-adsorption to iron and manganese hydroxides and oxides once oxidizing conditions are re-established.

**Zinc.** In the natural environment, Zn occurs exclusively in the divalent (2+) state. In dilute aqueous solutions, dissolved Zn commonly occurs as hydrated ions, metal-inorganic complexes, or metal-organic

complexes (*Framework for Metals Risk Assessment* [EPA 120/R-07/001]). The relative abundance of hydrated Zn species is strongly pH-dependent. Below a pH of about 6, the stability of hydrated Zn species is minimal and occurs primarily as the Zn2+ ion (*Chemical Equilibria in Soils* [Lindsay, 1979]; *Use of Apatite for Chemical Stabilization of Subsurface Contaminants Final Report* [Bostick et al., 2003]). At pH greater than 6, hydrated species increase in abundance, and at a pH above about 7.5, the neutral species Zn(OH)2 predominates (*Use of Apatite for Chemical Stabilization of Subsurface Contaminants Final Report* [Bostick et al., 2003]). Generally, the complexing of Zn with the common anions chloride, nitrate, and phosphate do not contribute substantially to the solubility of this metal in groundwater (*Chemical Equilibria in Soils* [Lindsay, 1979]). Sulfate, however, forms a relatively stable neutral complex with Zn (ZnSO4). The formation of this complex can increase the solubility and mobility of Zn in sulfate-rich soil solutions. However, under sulfate reducing conditions, the precipitation of very low-solubility Zn sulfide phases can drive the concentrations of Zn to very low levels.

The solubility of Zn in oxidizing groundwater is primarily limited by sorption onto clays and iron oxyhydroxides. As described above for lead and zinc, zinc can be released into groundwater by the reductive dissolution of iron oxy-hydroxides. Also as described for lead and cadmium, zinc solubilized by the ISRM and the treatability studies, will be relatively quickly re-adsorbed if transported into more oxidizing sections of the Hanford aquifer.

**Copper.** Copper (Cu) has an aqueous chemistry that is generally similar to that of Cd, and Zn (*Chemical Equilibria in Soils* [Lindsay, 1979]). However, unlike Cd and Zn, Cu does not occur strictly as a divalent ion. In aerobic systems, divalent copper (Cu2+) is the dominant valence state while Cu+ predominates under more reducing conditions (Figures 4-112 and 4-113). Solution and soil chemistry strongly influences the speciation of copper in ground-water systems. Typically, under oxidizing, organic-poor and moderately alkaline systems, CuCO3 is the dominant soluble species of copper (Figure 4-112). However, the cupric ion (Cu2+) (the most toxic species of copper) and the hydroxide complex Cu(OH)2, predominate under more acidic and higher pH oxidizing environments, respectively (*Remediation of Metals-Contaminated Soil and Groundwater* [Evanko and Dzombak,1997]). Under moderately oxidizing to moderately reducing and circum-neutral pH conditions, Cu+ concentrations in groundwater may be limited by the precipitation of Cu2O (see cuprite in Figure 4-112). Under sulfate reducing conditions, the insoluble phase CuS(s) will precipitate, greatly limiting the solubility of copper.

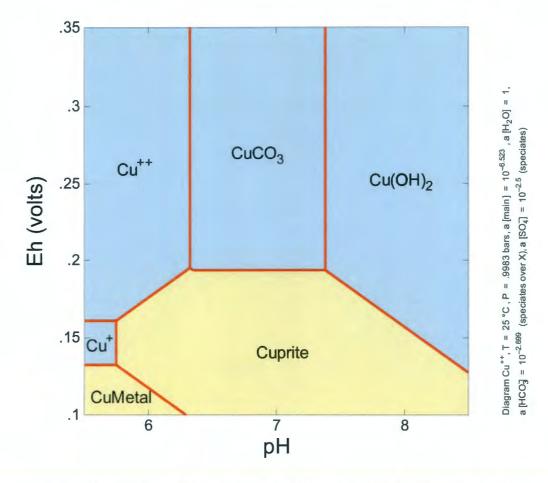


Figure 4-112. Speciation of Copper under Oxidizing to Moderately Reducing Conditions

Copper mobility in oxidizing groundwater is typically limited by sorption to particulate organic material and mineral surfaces in aquifers. As with Cd and Zn, copper ions sorb strongly to iron oxy-hydroxides over a wide range of pH values (Surface Complexation Modeling Hydrous Ferric Oxide [Dzombak and Morel, 1990]). Consequently, as with Cd and Zn, slightly elevated levels of Cu have occasionally been detected near the ISRM, where the natural iron oxides in the aquifer underwent reductive dissolution due to the injection of sodium dithionite. However, to a greater extent than Cd or Zn, Cu forms very strong aqueous complexes with humic acids (Figure 4-113). The tendency of Cu to form stable complexes with soluble humic compounds, increases as pH increases and with decreasing ionic strength (Remediation of Metals-Contaminated Soil and Groundwater [Evanko and Dzombak, 1997]). Consequently, the presence of elevated concentrations of humic acids in groundwater that has undergone bio-remediation, may result in longer-lived increases in the mobility of copper. Ultimately, however, the reestablishment of oxidizing aquifer conditions should eliminate the increased solubility and mobility of copper in the vicinity of the ISRM or bio-stimulation test areas.

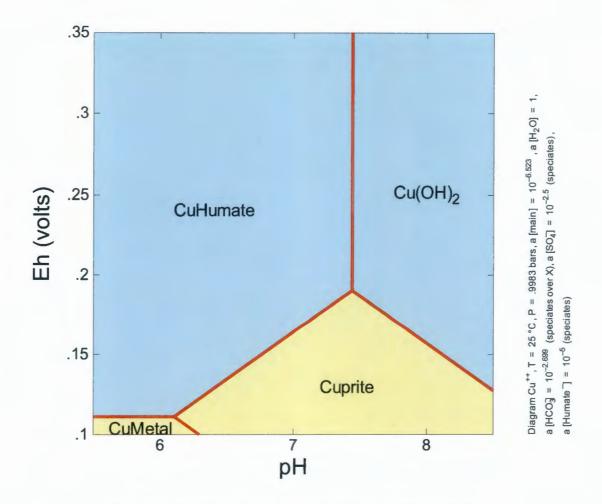
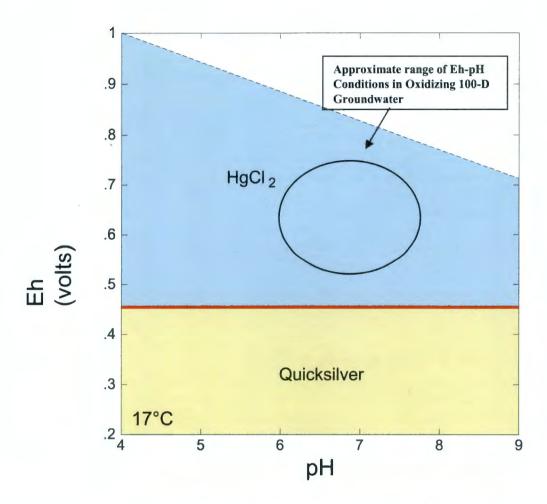


Figure 4-113. Copper Speciation in the Presence of Humic Acid

**Mercury**. Mercury (Hg) is stable in the divalent state in oxidizing groundwater with a circum-neutral pH (e.g. Hanford Formation Groundwater) and commonly forms strong, potentially mobile, aqueous complexes with chloride (Figure 4-114). In the presence of sulfide, Hg <sup>2+</sup> will precipitate as very low solubility mercury sulfide (HgS). At sufficiently reducing conditions, Hg is stable in the environment in the zero valent (metallic) form, commonly referred to as Quicksilver (Figure 4-114).

Divalent mercury is strongly sorbed by iron oxy-hydroxides that are commonly found in oxidizing aquifers ("Modeling the Adsorption of Mercury(II) on (Hydr)Oxides .1. Amorphous Iron-Oxide and Alpha-Quartz" [Tiffreau, et al., 1995]). As with other divalent heavy metals, Hg that is sequestered by iron oxy-hydroxides s can be mobilized into the aqueous phase by the reductive dissolution of iron oxy-hydroxides in an aquifer where reducing conditions have been imposed And as also occurs for other heavy metals, divalent Hg will be strongly re-adsorbed once oxidizing conditions in the aquifer are re-established or if the Hg is transported outside of the reducing zone of an aquifer. Although detectable concentrations of Hg may have been locally mobilized at 100-D and 100-H by the ISRM and the treatability tests, it should be quickly re-adsorbed by iron oxy-hydroxides once transported outside the areas in the aquifer where reducing conditions were imposed.



Note: P = 1.0 Atm, DO = 8.0 mg/L, Mercury = 0.02 mg/L, Chloride = 14.5 mg/L

Figure 4-114. Mercury Speciation as a Function of Eh and pH

**Thallium**. Thallium in groundwater systems typically occurs in the monovalent redox state (Tl I) and the predominant aqueous species is the monovalent ion (Tl +). In acidic and/or highly oxidizing aqueous systems, thallium may be stable in the trivalent valence state (Tl III). At a pH below about 3, the predominant trivalent aqueous species is the Tl 3+ion. At progressively higher pH conditions (from pH 4 to 12), the dominant aqueous speciation of Tl III progressively changes from Tl 3+ to cationic, neutral, and anionic hydroxy species (e.g., TlOH2+,Tl(OH)4 -).

Monovalent Tl has an ionic radius similar to K+ and is enriched in potassium feldspars relative to most other primary aquifer matrix materials. Thallium is also found as a trace element in cadmium, zinc, and iron sulfide ore minerals and, under sulfate reducing groundwater conditions, Tl+ will precipitate as a sulfide (*Environmental levels of thallium – Influence of redox properties and anthropogenic sources* [Karlsson, 2006]). Although thallium sulfide appears to be the only solubility limiting phase for Tl+ in groundwater, Tl+ is subject to sorption by materials in the aquifer matrix such as natural organic materials, clays, hydrous ferric oxides and manganese oxides. Of these sorptive phases, manganese oxides have the greatest potential to strongly and irreversibly sequester thallium. Manganese oxides have highly reactive and oxidizing surfaces that are known to catalyze the oxidation of Tl + to Tl+3 (Karlsson, 2006). Once Tl+ is oxidized to Tl 3+ at the surface of a manganese oxide, Tl 3+ behaves similarly to trivalent iron and aluminum and readily hydrolyzes, forming a low solubility hydroxide (Tl(OH)3).

The aqueous chemistry of thallium indicates that, once oxidizing conditions are re-established in the reducing sections of aquifer associated with the ISRM or test biostimulation areas, or if Tl+ migrates out of the existing reducing zones, Tl+ should be subject to rapid sorption by Mn(IV) oxides, oxidation to Tl+3 and precipitation as a low solubility hydroxide phase (Tl[OH]3). Consequently, any detectable concentrations of thallium in the groundwater at the 100-HR-3 OU should decline back to background levels, once the naturally oxidizing conditions are reestablished.

Summary and Conclusions. The elevated concentrations (relative to background) of dissolved iron, manganese, arsenic, mercury, thallium, cadmium, lead, zinc, copper, sulfate, nitrite, and bromide, detected within the 100-HR-3 OU are the result of the locally reducing aquifer conditions produced by the ISRM and the treatability tests that have been implemented at this OU. Owing to the limited scale of the biostimulation tests, the detected concentrations of the secondary contaminants associated with these tests are expected to rapidly decrease back to near background levels, once oxidizing conditions are reestablished in the treatment zones. A similar process is anticipated for the ISRM. However, owing to the much larger scale of this system, the effects of the ISRM will persist for a greater period.

The effective longevity of the ISRM treatment capacity was estimated to be 23 years from its completion (FY 2003 to FY 2026), and that parts of the barrier were depleted as early as 2007, it is probable that the secondary groundwater effects produced by the sodium dithionite-based ISRM (e.g., locally iron, manganese, sulfate, and arsenic concentrations) will return to near background levels by FY 2026.

### 4.5.14 Summary of Contamination in Groundwater at 100-D/H

The nature and extent of contamination in groundwater has been monitored extensively since 1997 to evaluate the implementation of the interim remedies. In 2009, an RPO was initiated to optimize and expand the pump-and-treat systems in 100-D/H. This effort resulted in installation of 70 production wells that provided additional information in support of this RI Report. In addition, the 10 RI characterization boreholes and the 17 RI characterization wells have provided significant new information that expands the general understanding of the nature and extent of contamination in groundwater.

The sampling and analysis of groundwater was conducted under the 100-D/H SAP (DOE/RL-2009-40, as modified by Change Notice for Modifying Approved Documents/Workplans In Accordance with the Tri-Party Agreement Action Plan, Section 9.0, Documentation and Records: Interim Action Monitoring Plan for the 100-HR-3 and 100-KR-4 Operable Units, DOE/RL-96-90, Rev. 0 [TPA-CN-298]). The RPO work was conducted under a separate SAP (Sampling and Analysis Plan for Installation of 100-HR-3 Groundwater Operable Unit Remedial Process Optimization Wells [DOE/RL-2009-09]). The collective body of information, including the annual monitoring information, indicates that the nature and extent of contamination in groundwater at 100-D/H is well understood in terms of the magnitude of the contamination present and the geography of the contaminant plumes.

Groundwater contamination statistics were calculated for the 100-D, Horn, and 100-H portions of 100-D/H. Cr(VI) is the largest single groundwater contaminant with plumes in 100-D, Horn, and 100-H. The areal extent (in square kilometers) of the various contaminant plumes within 100-D/H are shown in Table 4-19. In 100-D, the Cr(VI) plume is subdivided into the 100-D southern and northern plumes. The 100-D southern plume originates near the 105-DR Reactor near the 100-D-12 and 100-D-100 waste sites. Figure 4-70 shows the relationship of the Cr(VI) plume to the potential source areas. The 100-D southern plume contains the highest concentrations of Cr(VI) at the Hanford Site with concentrations in excess of 60,000  $\mu$ g/L (69,700  $\mu$ g/L in Well 199-D5-122 in August 2010). Some vertical stratification of Cr(VI) is observed in the unconfined aquifer in the 100-D southern plume, but the stratification is not consistent throughout. RI data indicated that in the 100-D southern plume, where there are moderately high concentrations of Cr(VI), high concentrations are present at the bottom of the unconfined aquifer.

The 100-D northern plume is located closer to the 105-D Reactor near portions of the piping system that transmitted concentrated sodium dichromate from the unloading station to the head house next to Building 183-D. Figure 4-70 shows the relationship of the plume to the nearby waste sites. A single waste site has not yet been identified that coincides with the area of higher concentrations at the 100-D northern plume. There is, therefore, some potential that leakage from the 182-D Reservoir has separated a single larger plume into the two distinct areas. Leakage from the reservoir is apparent in the geochemistry from nearby Well 199-D5-33, which has a geochemical signature similar to the Columbia River (Section 3.8).

A large diffuse plume of Cr(VI) is located in the Horn between 100-D and 100-H (Figures 4-72 and 4-73). Groundwater from the unconfined aquifer underlying the Horn generally exhibits much lower Cr(VI) concentrations than are present in the 100-D plumes, although concentrations at many locations still exceed the state surface water quality standard of 10  $\mu$ g/L and the 2007 MTCA ("Groundwater Cleanup Standards" [WAC 173-340-720]) level of 48  $\mu$ g/L. The Horn has very few waste sites, and the Cr(VI) detected in shallow groundwater likely migrated across the Horn with groundwater flow from 100-D, rather than having originated from local releases.

The Cr(VI) plume in the unconfined aquifer at 100-H (Figures 4-72 and 4-73) is characterized by much lower concentrations than the 100-D plumes, and has mostly been remediated in this area. Cr(VI) concentrations in the unconfined aquifer are less than 100  $\mu$ g/L; however, most portions of the plume underlying 100-H exceed the state surface water quality standard of 10  $\mu$ g/L. Figure 4-80 shows the relationship of primary sources to the Cr(VI) plume. In the unconfined aquifer, higher groundwater flow rates and the relative success of the interim remedy pump-and-treat system in this area have resulted in low remaining concentrations.

Cr(VI) has been identified underlying 100-H within the first water-bearing unit of the RUM, with the highest concentrations near the Columbia River, as well as in one location of the Horn near 100-D. The contamination within the RUM at 100-H is likely a result of the high hydraulic head conditions created from the groundwater mound at the 116-H-7 Retention Basin during reactor operations. The pressure of the mound pushed the contaminated groundwater into the lower unit. As discussed in Chapter 3, the material of the RUM between the unconfined aquifer and the first water bearing unit within the RUM consists of more transmissive material, which also appears to be thinner at 100-H, as compared to 100-D.

The details of Cr(VI) in groundwater were described in Section 4.5. In addition, the rebound testing conducted in 2009 (*Aquifer Testing and Rebound Study in Support of the 100-H Deep Chromium Investigation* [SGW-47776]), resulted in an increase of Cr(VI) concentrations in the RUM Well 199-H4-12C, which does not appear to be hydraulically connected to the unconfined aquifer (based on current data). At Well 699-97-48C, high hydraulic head would have been present as a result of discharges to the 116-DR-1&2 Trench and retention basins at 100-D. As discussed in Chapter 3, the presence of the Ringold Formation unit E in locations just northeast of the trenches appears to have resulted in a preferential pathway across the Horn. The geologic conditions also would have been conducive to high hydraulic head near Well 699-97-48C.

Several other constituents are important in groundwater at 100-D/H. The interim action RODs (100-HR-3 and 100-KR-4 Interim ROD [EPA/ROD/R10-96/134] and 100-HR-3 Interim ROD Amendment [EPA/AMD/R10-00/122]) listed the following potential co-contaminants at 100-D/H: nitrate, strontium-90, tritium, uranium, and technetium-99. These co-contaminants have been monitored extensively in the years since these RODs were issued. Technetium-99 is present at very low levels and does not warrant further classification as a co-contaminant, but continued monitoring is required through the current RCRA permit. Uranium levels are below the DWS, but increased from concentrations around

 $10 \mu g/L$  to a concentration of 28.9  $\mu g/L$  in Well 199-H4-3, in response to unusually high water table elevations during 2011.

The nitrate plumes are defined as areas greater than the DWS (45,000 µg/L), and overlap a portion of the Cr(VI) plumes at 100-D. The south nitrate plume extends over to the 118-D-3 waste site east of the 105-DR Reactor. The northern nitrate plume extends from the 105-D Reactor up to the area of the retention basins and west of the 116-DR-1&2 Trench. Nitrate concentrations in groundwater above the DWS in 100-H are limited to two small areas (Figure 4-97). The RI results confirmed the extent of the plumes in both reactor areas.

Strontium-90 is found in the unconfined aguifer at both 100-D and 100-H. A small plume has historically been monitored at 100-H in the area east of the 105-H Reactor near the 116-H-7 Retention Basin and the 116-H-1 Trench (Figure 4-105). Both of these are likely historical release points for Sr-90-contaminated water. The strontium-90 plume at 100-H exhibits small seasonal variations apparently related to the water table elevations. Strontium-90 was detected in RI Well 199-H3-6 at 8.2 pCi/L. At 100-D, strontium-90 is found in groundwater near 105-D Reactor and the 116-D-1A and 116-D-1B wastewater trenches. These are both likely historical release points for Sr-90 contaminated water; the fuel storage basin at 105-D Reactor may have leaked contaminated water to the vadose zone and the wastewater trenches received fuel storage basin overflow and other radiologically-contaminated wastewater. Sr-90 has been detected in groundwater near 105-D Reactor for about 20 years, with persistent detections in Well 199-D5-12 at concentrations as high as 52.6 pCi/L in March 1990. This well was decommissioned in 2002 when groundwater levels dropped below the pump intake level, but the well had not been sampled since late 1999. RI Well 199-D5-132 (C7622, Well 4) was installed to replace this well and provide an evaluation point for strontium-90 near 116-D-1A trench. Elevated levels of strontium-90 were detected in borehole groundwater samples at all depth intervals in Well 199-D5-132 (Table 4-25) at concentrations consistent with those historically detected in Well 199-D5-12. Persistent detections of Sr-90 in groundwater near the 107-D and 107-DR Retention Basins have declined to below the DWS in recent years. Discontinuous low-level detections of Sr-90 have been measured in groundwater near 105-DR Reactor.

As discussed in Section 4.4.3.2, tritium has been detected historically in the unconfined aquifer at concentrations exceeding the DWS value of 20,000 pC/L near the ISRM barrier (Figure 4-109). The plume has been documented as being a remnant from the 100-N tritium plume associated with the 1325-N Crib. Concentrations in the unconfined aquifer near that area have since declined to less than the DWS. During the RI, tritium was detected in borehole groundwater samples from Wells 199-D5-132 and 199-D5-133 at 1,000 and 10,000 pCi/L, respectively, associated with the fuel storage basin and 100-DR-1. The groundwater sample from Well 199-D3-5 had a maximum detection of 17,000 pCi/L, likely associated with a nearby burial ground. At RI Well 199-D6-3, tritium was detected in a borehole groundwater sample at 20,000 pCi/L. However, a groundwater sample collected from the completed well in 2011 was 2,600 pCi/L, which introduces uncertainty regarding actual tritium concentrations in the unconfined aquifer at this location.

Small amounts of other constituents are present in the unconfined aquifer underlying 100-D/H. Those that were identified in the groundwater include zinc, carbon tetrachloride, chloroform, and sulfate. Zinc shows sporadic values greater than the aquatic limit (91  $\mu$ g/L) at several wells in 100-D/H. Carbon tetrachloride is found in very small amounts. The carbon tetrachloride overlaps a portion of the Cr(VI) plumes. Elevated chloroform was detected in groundwater from several wells within the 100-D north Cr(VI) plume. Sulfate is present in the unconfined aquifer at concentrations exceeding the secondary DWS of 250,000  $\mu$ g/L only at or downgradient of the ISRM barrier, where it is a byproduct of barrier chemical placement. Sulfate is detected in the unconfined aquifer in other areas underlying 100-D associated with sulfuric acid use. Additional analytes, such as antimony, cadmium, cobalt, silver, and nickel, were also

identified in groundwater; however, these analytes had infrequent detections, which result in uncertain status. All of these analytes were evaluated in the risk assessment and are discussed further in Section 4.4 and Chapter 6.

In conclusion, the nature and extent of contamination in groundwater at 100-D/H is complex. The major contaminant in groundwater is Cr(VI), which covers an area in excess of 7 km² of unconfined aquifer. Delineation of the plume boundaries is fairly well understood. To the southwest, Well 199-D3-5 was intended to delineate the plume along that boundary, but Cr(VI) was identified in borehole groundwater samples during drilling. Therefore, as part of the RD/RAWP or remedy implementation, additional delineation may be needed to ensure capture and/or treatment of the entire southern plume. Underlying 100-H, Cr(VI) contamination is present in the first water-bearing unit of the RUM, but the plume boundaries have not been fully delineated in that area to the south and southwest. Contamination is also present in one well located in the Horn (Well 699-97-48C), near 100-D. Other contaminants (primarily metals) have been detected and are evaluated in the risk assessment and discussed in Section 4.4 and Chapter 6.

# 4.6 Evaluation of Potential Effects on the Columbia River Adjacent to 100-D/H

Appendix L presents an evaluation of contaminants in riparian and nearshore media and the Columbia River. This evaluation addresses, on a reactor area basis, the potential for Hanford Site contaminants in soil or groundwater to migrate to riparian or nearshore areas or to the Columbia River at concentrations that could be of concern to ecological receptors.

The Appendix L evaluation supplements the analysis of the River Corridor-wide ecological risks presented in the ERA (RCBRA, Volume 1 [DOE/RL-2007-21]). The ERA identifies on a site-wide basis some contaminants of ecological concern (COECs) in riparian and nearshore media (soil, sediment, and water) that could warrant further evaluation.

Appendix L also addresses COECs identified in the Columbia River Component (CRC) ERA (DOE/RL-2010-117, Volume I), specifically those identified for 100-D/H. The following text describes the results of the two risk assessments, including the types of data collected to complete the assessments.

Table 4-30 lists the combined COECs from both the RCBRA (DOE/RL-2007-21) and the CRC (DOE/RL-2010-117). The evaluation of the HHE risk presented in the CRC (DOE/RL-2010-117, Volume II) addresses all the data collected throughout the Hanford Reach and downstream to McNary Dam, as directed in the Columbia River RI Work Plan (DOE/RL-2008-11). Chapters 6 and 7 summarize the Appendix L analysis, including results regarding which, if any, of the following COECs could be attributed to sources within the 100-D or 100-H.

COEC	Receptors	Media
Aluminum <sup>1</sup>	Fish	Pore Water
	Aquatic Invertebrates	
	Aquatic Plants	
Arsenic <sup>2</sup>	Terrestrial Plants	Riparian Soil
Cadmium 2	Aquatic Plants and Invertebrates	Sediment
Chromium 1	Fish	Pore Water
	Aquatic Invertebrates	

Table 4-30. Riparian, Nearshore, and Riverine COECs from the RCBRA and CRC

Table 4-30. Riparian, Nearshore, and Riverine COECs from the RCBRA and CRC

COEC	Receptors	Media
	Aquatic Plants	
Chromium 1,2	Aquatic Plants and Invertebrates and the Bufflehead	Sediment
Chromium <sup>2</sup>	Terrestrial Plants and Invertebrates	Riparian Soil
Cr(VI) 1,2	Aquatic Plants and Invertebrates	Sediment
Cr(VI) 1,2	Fish	Pore Water
	Aquatic Invertebrates	
	Aquatic Plants	
Lead 1	Fish	Pore Water
	Aquatic Invertebrates	
	Aquatic Plants	
Lead <sup>2</sup>	Terrestrial Plants	Riparian Soil
Manganese <sup>2</sup>	Aquatic Plants and Invertebrates	Sediment
Manganese <sup>2</sup>	Aquatic Plants and Invertebrates	Pore Water
Mercury <sup>2</sup>	Terrestrial Invertebrates	Riparian Soil
Nickel 1	Fish	Pore Water
	Aquatic Invertebrates	
	Aquatic Plants	
Nitrate 1	Fish	Pore Water
	Aquatic Invertebrates	
	Aquatic Plants	
TPH-Diesel <sup>2</sup>	Terrestrial Invertebrates	Riparian Soil
Uranium <sup>2</sup>	Aquatic Plants and Invertebrates	Pore water
Zinc <sup>2</sup>	Terrestrial Plants and Invertebrates and Kingbirds	Riparian Soil

#### Notes:

Evaluation on whether 100-D/H represents a potential source is presented in Appendix L.

- 1. COECs presented in the executive summary of the CRC (DOE/RL-2010-117)
- 2. COECs presented in Sections 8.4 and 8.5 of the RCBRA (DOE/RL-2007-21)

COEC = contaminant of ecological concern

CRC = Columbia River Component Risk Assessment, Volume 1: Screening Level Ecological Risk Assessment

(DOE/RL-2010-117)

RCBRA = River Corridor Baseline Risk Assessment, Volume 1: Ecological Risk Assessment (DOE/RL-2007-21)

## 4.6.3 Summary of Results and Conclusions of RCBRA and CRC

The RCBRA (DOE/RL-2007-21) evaluated ecological risks at 48 nearshore study sites potentially affected by contamination from Hanford Site sources in comparison to reference sites. Study sites were selected in areas where known contaminated groundwater plumes enter the Columbia River and in areas between the plumes. Twenty-two COPECs were identified for the nearshore environment and sixteen of these (all inorganics) were identified for further consideration. The RCBRA (DOE/RL-2007-21) concluded that across the Hanford Reach of the Columbia River (that is, River Corridor-wide), five COPECs are COECs (cadmium, chromium, Cr(VI), manganese, and uranium) in the nearshore

environment that may present an unacceptable level of risk for one or more of the assessment endpoint entities (aquatic plants, aquatic invertebrates, amphibians, fish, and wildlife). These results are based primarily on the comparisons of COPEC concentrations to toxicity benchmarks, measures of exposure and effects in biota, or the results of wildlife exposure analyses (RCBRA Report [DOE/RL-2007-21], Volume 1).

The RCBRA (DOE/RL-2007-21) also evaluated ecological risks at 18 representative riparian study sites located adjacent to, or where they may be directly affected by, known contaminated media (that is, groundwater seeps, soil, and sediment). In addition, data from the 100-B/C area pilot study and the 100-NR-2 ecological study were evaluated. As with the nearshore environment, 22 COPECs were identified for the riparian environment. The RCBRA (DOE/RL-2007-21) identified 9 of the identified 22 COPECs (arsenic, chromium, copper, lead, mercury, selenium, TPH-diesel, vanadium, and zinc) as possibly presenting some level of risk for one or more of the assessment endpoint entities (terrestrial plants, invertebrates, and wildlife). This is based on soil bioassays, comparison of COPEC concentrations to plant or terrestrial invertebrate benchmarks, or the results of wildlife exposure analyses. However, conclusions in the RCBRA (DOE/RL-2007-21) were that on a River Corridor-wide basis (combined 100 and 300 Areas), only six of these COPECs should be considered COECs (arsenic, chromium, lead, mercury, TPH-diesel, and zinc). Appendix L discusses these RCBRA-specified COECs with respect to ecological risk within 100-D/H.

The CRC (DOE/RL-2010-117, Volume 1) included an ecological risk assessment that combines both screening and baseline elements. Abiotic media were compared to screening benchmarks for surface water, sediment, and pore water to identify COPECs. Soil concentrations were compared to plant and invertebrate benchmarks, while desktop food web models were used to evaluate risks to wildlife. A baseline assessment was conducted to assess risk to fish using tissue residue data. The CRC (DOE/RL-2010-117, Volume 1) concluded there were eight COECs (aluminum, chromium, Cr(VI), lead, manganese, mercury, selenium, and uranium) within pore water, surface water, island soils, and sediment. The evaluation included distinct conclusions for the reach adjacent to the 100 Area versus those for the reach adjacent to the 100-D/H Source OUs. Six COECs were identified for the 100-D/H Source OUs, as presented in Table 4-30. Appendix L discusses these CRC-specified COECs with respect to ecological risk within the 100-D/H Source OUs.

### 4.6.4 Columbia River Surface Water, Pore Water, and Sediment Investigation

In 2004, a process was established to compile, classify, and manage environmental data (for example, surface water and sediment) associated with the Columbia River in Columbia River Component of the River Corridor Baseline Risk Assessment: Basis and Assumptions on Project Scope (DOE/RL-2004-49). The CRC database was created because of these efforts and was documented in Existing Source Information Summary Report Compilation/Evaluation Effort: December 2004 to September 2005 (WCH-64). The subsequent Columbia River Component Data Evaluation Summary Report (WCH-91) described the activities that were undertaken to evaluate the data collected in the compilation effort and to assist in defining the extent of Hanford Site-related contamination. The compiled data were used to identify potential data gaps in the spatial, temporal, and chemical composition of the existing dataset. The Columbia River Component Data Gap Analysis (WCH-201) presented the results of that analysis and provided the foundation for the sampling plan that was documented in the Columbia River RI Work Plan (DOE/RL-2008-11).

The scope of the Columbia River RI Work Plan (DOE/RL-2008-11) and *DQO Summary Report for the Remedial Investigation of Hanford Site Releases to the Columbia River* (WCH-265) included the following fieldwork component, which has generated data necessary to fill data gaps in the understanding

of current conditions in the Columbia River. The data from the field activities were evaluated in both ecological and human health risk assessments reported in the CRC (DOE/RL-2010-117).

Sampling to fulfill the needs defined in the Columbia River RI Work Plan (DOE/RL-2008-11) was initiated in October 2008 and completed in June 2010. Media sampled included surface water, pore water, sediment (shoreline, shallow, cores), island soil, and six species of fish. The results of the biota sampling are discussed in Appendix L and Section 4.6.1. The RI field activities associated with the collection of sediment, river water, and island soil in the Columbia River adjacent to and downstream from the Hanford Site and in nearby tributaries are documented in Field Summary Report for Columbia River RI (WCH-352). Field Summary Report for Columbia River RI (WCH-352) describes the sampling locations, identifies samples collected, and describes modifications and additions made to the SAP that was provided as Appendix A to the Columbia River RI Work Plan (DOE/RL-2008-11). Groundwater upwelling field activities and data collection are documented in the Columbia River RI Report (WCH-380).

Groundwater Upwelling Investigation at 100-D/H. Groundwater beneath the Hanford Site discharges to the Columbia River via seeps and upwelling to the riverbed. This flow path for groundwater provides a means for transporting Hanford Site-associated contaminants that entered the groundwater from past waste disposal practices to the Columbia River. As discussed in Section 2.1.7 of this report, the nearshore groundwater conditions are directly affected by river stage. The greatest contaminant flux and highest concentrations at exposure locations are postulated to occur during periods of low river stage. During this period, the hydraulic gradient toward the river is greatest and mixing between river water and groundwater is minimal.

Sediment samples collected from the locations shown on Figures 2-5 through 2-8 were analyzed for a range of radiological and nonradiological analytes as described in Table 2-5. Sediment samples were obtained as close to the pore water sample locations as reasonably possible, with a preference given to locations with fine sediment deposits. Sample volume was limited in some locations because of the dominance of cobbles on the riverbed. In locations where sediment sample volume was limited, not all analyses could be performed at each location. Information on the number of sediment samples collected and the period in which they were obtained is presented in Table 2-7. Additional sediment, island soil, and surface water samples were collected in areas identified in *Columbia River Component Data Gap Analysis* (WCH-201) and the Columbia River RI Work Plan (DOE/RL-2008-11).

To address the uncertainty related to the level of contamination entering the Columbia River via upwelling, including contaminant transport mechanisms, data were collected near 100-D/H. Pore water, surface water, and sediment sampling in the Columbia River was conducted in 2009 and 2010, as outlined in the Columbia River RI Work Plan (DOE/RL-2008-11). The following paragraphs discuss the sediment, surface water, and pore water samples presented in the CRC (DOE/RL-2010-117, Volume I) as described in DQO Summary Report for the Remedial Investigation of Hanford Site Releases to the Columbia River (WCH-265) and Sampling and Analysis Instructions for the Remedial Investigation of Hanford Site Releases to the Columbia River (WCH-286) as these data relate to 100-D/H. The aquifer tube results are presented and discussed in Section 4.5.

The influence of contaminants on the water quality immediately above groundwater upwelling locations was determined by taking surface water samples. River water was collected concurrently during pore water sample collection at approximately 0.3 m (12 in.) above the riverbed. At 100-D/H, surface water sample analysis at all sample locations included the analytes listed in Table 2-5. Information on the number of surface water samples collected and the period in which they were obtained is presented in Table 2-7.

To determine if surface water or groundwater was being collected, specific conductance and temperature were used as indicators. The specific conductance or conductivity in the Columbia River is typically lower (130 to 145  $\mu$ S/cm) than groundwater (400 to 600  $\mu$ S/cm). In addition, in this region of the Columbia River, surface water temperatures typically range from approximately 0.5 °C (33 °F) in the winter months to more than 27 °C (80 °F) during the late summer months, whereas groundwater typically stays between 7 °C (45 °F) and 15 °C (60 °F) (Columbia River RI Report [WCH-380]).

**Phase II(a) and Phase II(b) Sampling.** Pore water samples collected as part of the Phase II(a) groundwater upwelling investigation defined in the Columbia River RI Work Plan (DOE/RL-2008-11) helped to delineate areas of groundwater upwelling into the river bottom. Measurements of conductivity and temperature in pore water were used to guide the selection of Phase II(b) stations that were sampled for indicator contaminants. As described in Section 2.1.7, Cr(VI) was the indicator contaminant in both the 100-D and 100-H areas. Further discussion of this investigation is found in the Columbia River RI Report (WCH-380). Additional discussion of the analytical results from these areas can be found in Hanford Site Releases Data Summary (WCH-398).

Conductivity measurements made at all of the Phase II(b) sample locations near 100-D indicated the presence of groundwater. Of the 30 sites where pore water was measured for Cr(VI), 11 sample results exceeded the state surface water quality standard (10  $\mu$ g/L). The two highest Cr(VI) pore water concentrations (112 and 331  $\mu$ g/L) were collected from two separate regions with water depths less than 0.9 m (3 ft) below the low water mark. The highest Cr(VI) pore water concentration (331  $\mu$ g/L) was located just upstream from the 181-D River Pump Station where an aquifer tube showed a concentration of 380  $\mu$ g/L and a well inland had a concentration of 700  $\mu$ g/L. The second highest concentration (112  $\mu$ g/L) was located about 9.7 m (32 ft) off shore from an area where Cr(VI) groundwater plume estimates of 100  $\mu$ g/L are found in the wells.

Thirty Phase II(b) sample locations were selected near 100-H. Pore water conductivity measured during Phase II(b) showed the presence of groundwater at all locations. Fifteen Cr(VI) sample results exceeded the state surface water quality standard (10  $\mu$ g/L; results ranged from 12 to 46  $\mu$ g/L). Three of these fifteen locations were downriver near the White Bluffs Townsite boat launch. One station had a strontium-90 value of 6.78 pCi/L, which is comparable to the predicted groundwater plume concentration (8 pCi/L) in that area.

**Phase III Sampling.** Phase III sample locations were a subset of the previous sample locations for characterization sampling and analysis of pore water, surface water (0.3 m [1 ft] above the riverbed), and collocated sediment for a broad range of analyses defined in the Columbia River RI Work Plan (DOE/RL-2008-11).

Sediment samples were collected as close to the pore water sample location as reasonably possible, with a preference given to locations with sediment deposits. Bulk sediment Cr(VI) concentrations ranged from 0.2 to 4.7 mg/kg with the highest concentration found in 100-D, which corresponds to the concentrations as measured in pore water. Additional Phase III analytical result discussions can be found in Hanford Site Releases Data Summary (WCH-398).

Six sample locations were selected for Phase III sampling in 100-D. Samples from pore water and proximal river water were collected at all six sites. Pore water conductivity values ranged from 213  $\mu$ S/cm to 560  $\mu$ S/cm. Typical groundwater conductivity values range from 400  $\mu$ S/cm to 600  $\mu$ S/cm. Laboratory results for surface water Cr(VI), total uranium, and strontium-90 were below detection limits. Pore water sample results for Cr(VI) ranged from 9 to 640  $\mu$ g/L, with the maximum value found at station T100D3A where a high value of 331  $\mu$ g/L was detected during Phase II(b) (Columbia River RI Report [WCH-380, Rev. 1]). A single detection of strontium-90 (1.5 pCi/L) was reported at a station along the

Hanford Site shoreline adjacent to the 100-D island. Tritium was also detected from 353 to 14,100 pCi/L with the maximum level (14,100 pCi/L) found in an area adjacent to the 100-D strontium-90 groundwater plume.

Six sample locations were selected for Phase III sampling in 100-H. Samples from pore water and proximal river water were collected at all six sites. Pore water conductivity values ranged from 184 to 343  $\mu$ S/cm, perhaps indicating some degree of suppression or mixing as a result of the river stage at the time of the Phase III measurements. Typical groundwater conductivity values range from 400 to 600  $\mu$ S/cm. A site upriver of the 100-H Reactor area yielded the maximum pore water conductivity value during Phase III. Laboratory results for Cr(VI), total uranium, and strontium-90 in surface water were not detected during Phase III. Pore water results for Cr(VI) ranged from 7 to 50  $\mu$ g/L, with the maximum value found at the station upriver of 100-H. Tritium was also detected over a range of 454 to 1,250 pCi/L, with the maximum found at the same upriver station as the Cr(VI) maximum. The amounts of strontium-90 detected in pore water results were all below detection with the exception of a 6 pCi/L result from a location adjacent to the 100-H strontium-90 groundwater plume (Columbia River RI Report [WCH-380, Rev. 1]).

**Sediment and Surface Water Samples near 100-D/H.** In addition to the sampling performed during the groundwater upwelling investigation, samples of sediment, surface water, and island soil were obtained from select locations to develop a better understanding of the nature and extent of potential contaminants released from the Hanford Site and to support subsequent human health and ecological risk assessments.

For 100-D/H, the following sampling efforts were conducted:

- A shallow sediment core was collected near the 181-D river pump station.
- Several shallow sediment samples were collected from the downstream end of the 100-D island, and
  further downstream from the island both shallow sediment and shoreline sediments were taken at
  locations conducive to sediment deposition in the river.
- Shallow sediments were collected, as well as three surface water samples, along the Grant County shoreline of the river.
- Ten soil samples and several shoreline sediment samples were collected from Island 3 (upriver from 100-H).
- Soil and shoreline samples were collected from Locke Island (adjacent to and downstream from 100-H).

The analytical results for these samples are presented in Hanford Site Releases Data Summary (WCH-398). The CRC (DOE/RL-2010-117) presents an evaluation of the HHE risk represented by all the data collected, as directed in the Columbia River RI Work Plan (DOE/RL-2008-11). This evaluation addresses all the data collected throughout the Hanford Reach and downstream to McNary Dam.

**Conclusions.** The fieldwork associated with the Columbia River RI was completed in accordance with the requirements defined in the Columbia River RI Work Plan (DOE/RL-2008-11). Based on the data collected, it was confirmed that groundwater upwelling does occur in the Columbia River. The potential impacts to ecological and human receptors were evaluated in the CRC risk assessments (DOE/RL-2010-117) and are discussed in Chapters 6 and 7.

### 4.6.5 Nature and Extent of Contamination in Riparian and Nearshore Areas

Evaluation of contaminants in riparian and nearshore media involved developing a CSM of the riparian and nearshore environment along 100-D/H (Appendix L). This CSM addressed, on a reactor area basis, the potential for Hanford Site contaminants in soil or groundwater to migrate to riparian or nearshore areas at concentrations that could be of concern to ecological receptors. The point of departure for this CSM was the analysis of the River Corridor-wide ecological risks presented in the RCBRA ERA (DOE/RL-2007-21, Volume I). The RCBRA identified on a sitewide basis some COECs in riparian and nearshore media (soil, sediment, and water) that could warrant further evaluation. Sources, fate and transport pathways, and exposure points were identified to provide a framework for evaluating sampling and analytical data in the riparian and nearshore area. Data characterizing riparian area soils, near-river groundwater, groundwater from aquifer tube samples, pore water samples, seep samples, sediments, and surface water integrated across the 100-D/H RI/FS and the RCBRA were evaluated to determine if Hanford Site contaminants could migrate to riparian and nearshore areas at concentrations posing an ecological risk or could have been responsible for the measured concentrations observed. The spatial distributions of contaminants across the different media were compared to determine if there might be transport from onsite soils and groundwater to riparian/nearshore areas.

Concentrations at exposure points in sediment and all aqueous media (groundwater, aquifer tubes, seeps, pore water, and surface water) were compared with ecological screening levels to identify contaminants posing an ecological risk. Concentrations of some metals in pore water and sediments were higher than screening levels for aquatic plants or invertebrates; however, these appeared to be unrelated to Hanford Site sources, based on the relative distribution of concentrations between near-river groundwater and nearshore media, or comparison with reference areas. Concentrations of total chromium and Cr(VI) in pore water were higher than AWQC and state surface water quality standard, and could be associated with Cr(VI) contamination in groundwater. Based on the results of the evaluation in Appendix L, with the exception of total chromium and Cr(VI), detected concentrations of contaminants in riparian or nearshore media are not reliably detectable at levels of ecological concern, or are not associated with contamination in soil or groundwater resulting from Hanford Site operations.

#### 4.7 Biota

This section summarizes ecological sampling or biological monitoring data that have been collected for 100-D/H. Biota data are useful to understand biological receptors, which are evaluated in Chapter 7.

Biota data from two main environmental sampling projects conducted at the Hanford Site were reviewed and summarized for this section. The SESP is a multimedia environmental surveillance project conducted by PNNL. The primary goal of the SESP is to measure concentrations of radionuclides and chemicals in environmental media to demonstrate compliance with applicable environmental quality standards and public exposure limits, and to assess environmental effects. Project personnel annually collect samples of ambient air, surface water, agricultural products, fish, wildlife, and sediments. Soil and vegetation samples are collected about every five years. SESP analytical capabilities include the measurement of radionuclides at environmental concentrations. In selected media, SESP can also measure environmental concentrations of nonradiological constituents including metals, anions, VOCs, and total organic carbon (TOC). The SESP sampling design is described in *Environmental Monitoring Plan United States Department of Energy Richland Operations Office* (DOE/RL-91-50).

Fish tissue has been a part of monitoring at the Hanford Site for many years, resulting in a variety of species and fish tissue in the database of historical samples. Within the historical fish tissue dataset, there is considerable inconsistency in species evaluated, tissue type (whole body, fillet, skin on, skin off), and analytes. Additionally, multiple collection and analysis approaches, as well as variability in species life

spans, are believed to have introduced significant variability in analytical results. Fish tissue sampling was part of the CRC HHRA (DOE/RL-2010-117, Volume II). The Columbia River RI Work Plan (DOE/RL-2008-11), DQO process (*Data Quality Assessment Report for the Remedial Investigation of Hanford Site Releases to the Columbia River, Hanford Site, Washington* (WCH-381) and SAP (*Sampling and Analysis Instruction for the Remedial Investigations of Hanford Site Releases to the Columbia River* (WCH-286) for the CRC (DOE/RL-2010-117, Volume II) defined a consistent sampling and analysis approach among species, tissue types, and analytes. Therefore, only fish tissue data from 2009 to 2010 were used in the CRC HHRA (DOE/RL-2010-117, Volume II); the 2009 to 2010 program focused on target fish species intended to be most representative of the exposure scenarios identified for the CRC HHRA (DOE/RL-2010-117, Volume II):

- Common carp (Cyprinus carpio)
- Mountain whitefish (Prosopium williamsoni)
- Walleye (Stizostedion vitreum)
- Smallmouth bass (Micropterus dolomieui)
- Bridgelip sucker (Catostomus columbianus)
- White sturgeon (Acipenser transmonatrus)

These six fish species are year-round resident fish that reflect a range of trophic levels and have a higher rate of harvest and consumption among the local population. As described in the Columbia River RI Work Plan (DOE/RL-2008-11), salmon were not sampled as part of this study because they spend most of their life cycle in the ocean as opposed to the Hanford Site Study Area.

For all species except sturgeon, fish tissue samples were composite samples composed of tissue from approximately five fish. Generally, five samples of each fish species were collected from each area, and each sample included separate fillet, carcass (which included the head and skeleton of the fish), and combined liver and kidney tissue for analysis. For carp, sufficient tissue mass was available to obtain separate liver and kidney samples. Fillet samples for all of these species except sturgeon were prepared with the skin on, because skin for these types of fish is often left on during preparation, and consumed. Sturgeon samples were not composited, and thus samples represent tissue from individual fish. Sturgeon fillet samples were collected with the skin off, and separate liver and kidney samples were prepared.

Biota data are also summarized from ecological samples collected to support the RCBRA ERA (DOE/RL-2007-21, Volume I). The primary goal of RCBRA is to evaluate current and potential future risks to the environment posed by releases of hazardous substances. RCBRA appraises relevant sources of contamination, exposure pathways, and contaminants for several environmental media and receptors including surface soil, vegetation, soil invertebrates, small mammals, and birds. RCBRA analytical capabilities include the measurement of radionuclides, metals, anions, SVOCs, herbicides, and pesticides at environmental concentrations, as well as physical properties (pH, moisture, particle size) in selected media. Most of the RCBRA environmental samples were collected in 2006 and 2007. The RCBRA sampling and analytical specifications are documented in the RCBRA SAP (DOE/RL-2005-42).

Figure 4-115 shows the SESP and RCBRA biota sample locations. The terrestrial plant and animal species collected and the tissues analyzed are as follows:

- Perennial vegetation: stems and leaves (combined)
  - Dominant shrub: current year's growth
  - Dominant grass: current year's growth
  - Balsamroot: leaves, roots

- Terrestrial invertebrate: whole body composites
- Mouse: whole body composites; kidney and liver (combined)
- Mule Deer: antler
- Bird: Western Kingbird organs, crop

Table H-23 in Appendix H summarizes plant tissue samples collected within 100-D/H for the SESP and RCBRA projects. Samples collected for RCBRA were analyzed for radioactive and nonradioactive constituents. The samples collected for SESP were analyzed for radionuclides and total uranium only. The table also shows a summary of plant tissue samples collected from several reference areas (unaffected areas) as a part of the RCBRA project. The reference samples were analyzed for the same suite of analytes as the RCBRA study site samples. The plant tissue sample results from the 100-D/H study sites are within the range of the results for the reference area samples.

Appendix H, Table H-24 summarizes the invertebrate tissue samples collected within 100-D/H for the RCBRA project. The samples were analyzed for metals and radionuclides only. Because of insufficient sample volumes, organic constituents were not analyzed. The table also shows a summary of invertebrate tissue samples collected from several reference areas (unaffected areas) as a part of the RCBRA project. The reference samples were analyzed for the same suite of analytes as the RCBRA study site samples. For the inorganic analytes, the invertebrate tissue sample results from the 100-D/H study sites are within the range of the results for the reference area samples with the exception of aluminum, arsenic, total uranium, lead, nickel, silicon, and zinc, which show slightly higher concentrations. For the radionuclides, the invertebrate tissue sample results from the 100-D/H study sites are within the range of the results for the reference area samples, except technetium-99 and uranium-233/234, which show slightly higher concentrations.

Appendix H, Table H-25 summarizes the mouse tissue samples collected within 100-D/H for the RCBRA project. The samples were analyzed for radioactive and nonradioactive constituents. The table also shows a summary of mouse tissue samples collected from several reference areas (unaffected areas) as a part of the RCBRA project. The reference samples were analyzed for the same suite of analytes as the RCBRA study site samples. For the inorganic analytes, the mouse tissue sample results from the 100-D/H study sites are within the range of the results for the reference area samples with the exception of boron, sodium, and tin, which show slightly higher concentrations. For the radionuclides, the invertebrate tissue sample results from the 100-D/H study sites are within the range of the results for the reference area samples with the exception of potassium-40 and radium-228, which show slightly higher concentrations.

Appendix H, Table H-26 summarizes two mule deer antler samples collected for SESP. The samples were analyzed for strontium-90 only. No anomalies were observed for strontium-90. There are no comparable reference samples for the mule deer antler samples.

Table H-27 in Appendix H, summarizes the western kingbird organ and crop tissue samples collected within 100-D/H for the RCBRA project. The samples were analyzed for metals and radionuclides only. Because of insufficient sample volumes, organic constituents were not analyzed. The table also shows a summary of bird tissue samples collected from several reference areas (unaffected areas) as a part of the RCBRA project. The reference samples were analyzed for the same suite of analytes as the RCBRA study site samples. For the inorganic analytes, the bird tissue sample results from the 100-D/H study sites are within the range of the results for the reference area samples with the exception of boron, phosphorus, and zinc, which show slightly higher concentrations. For the radionuclides, the invertebrate tissue sample results from the 100-D/H study sites are within the range of the results for the reference area samples with the exception of potassium-40, which shows slightly higher concentrations.

4-276

Figure 4-115. Location of SESP and RCBRA Biota Samples

### 4.8 Air

Atmospheric releases of radioactive materials from Hanford Site facilities and operations to the surrounding region are potential sources of human exposure. On the Hanford Site, radioactive constituents in air are monitored onsite near facilities and operations, at Sitewide locations away from facilities, and offsite around the Site perimeter, as well as in nearby and distant communities. As discussed in Section 2.1.6, Hanford Site contractors monitor radionuclide airborne emissions from Site facilities through several programs. The Near-Facility Environmental Monitoring Program measures concentrations of radionuclides in the ambient air on the Hanford Site near facilities and operations. The Hanford Site Environmental Surveillance Program measures the ambient air at Sitewide locations away from facilities, around the perimeter of the Site, and offsite in nearby and distant communities. In addition, emissions from stacks, vents, or other types of point sources are monitored individually by analyzing samples extracted from the outflow at each point of release. Currently, no point source releases are associated with 100-D/H.

The data collected by each program are used to assess the effectiveness of emission treatment and control systems and pollution management practices, and to determine compliance with state and federal regulatory requirements. Pollution management practices include controlling fugitive emissions during remediation and monitoring to ensure mitigation measures are adequate for emission control and worker exposure. Additional description of the ambient air sampling activities is available in the 2009 Sitewide Environmental Report (PNNL-19455). There were no notifications of air sample exceedances to WDOH for samples collected at 100-D/H in 2009. Air sample locations are shown on Figure 2-4.

# 4.9 Conceptual Site Model

The purpose of this CSM is to describe the features, events, and processes that resulted in the observed environmental contamination at 100-D/H and affect the future migration of existing contamination in soil and groundwater at the Hanford Site. The CSM relies on a comprehensive review of all available data, including field data if available, radiological surveys, process history, analogous site information, personal interviews, engineering drawings and as-builts, and any other available information. The CSM is based on the following:

- Primary sources of contamination are the liquids and solids that were used during reactor operations (Chapters 1 and 3).
- Physical features of the site, both natural and artificial, including soil, groundwater, surface water, climatic, and biologic features that affect the potential migration of contaminants and exposure to potential receptors (Chapter 3).
- Secondary sources (primarily vadose zone material or groundwater) that became contaminated as a
  result of releases of primary sources of contamination into the environment; these secondary sources
  resulted from operation and activities that have contributed to contamination of other environmental
  media (primarily groundwater and secondarily surface water or riparian soil) (Chapter 4).
- Description of the environmental pathways, driving forces, and transport mechanisms through which
  contaminants migrate from the reactor areas and associated waste sites through the ground to the river
  (Chapter 5).
- Potential exposure pathways and receptors for site contaminants (Chapters 6 and 7).

The resulting CSM integrates all of these elements to provide a basis for understanding contaminant fate and transport in the environment. This understanding is an important part of the RI/FS process and provides a technical basis for the description and understanding of Site conditions, assessment of the

actual and potential risks posed by Site conditions, and evaluation of the need for remedial action(s). A summary diagram illustrating the multiple aspects of the contamination condition at 100-D/H is shown on Figure 4-116. As indicated in this illustration, primary contaminant sources were released by numerous mechanisms, producing varying potential secondary sources. Contaminants are subject to numerous transport mechanisms and may reach potentially exposed receptors at multiple exposure points associated with the vadose zone, groundwater, and surface water.

The approach to presentation of the CSM in this section is to synthesize our knowledge of Site conditions and operating history to provide a description for understanding the interrelations of the various contaminant migration pathways. Chapters 1 through 4 provide a framework for the conceptualization and characterization process. These results are synthesized in Chapter 5 to describe the fate of contaminants in the system as they move through the vadose zone and aquifer to the river. Chapters 6 and 7 determine the ecological and human health risks posed by these contaminants from the distribution and amounts of contaminants present at potential exposure points. For those contaminants with an actionable risk, the CSM is used in Chapters 8 through 10 to identify appropriate remedial technologies and to evaluate remedial alternatives.

The FS identifies specific remedial technologies that are applicable to the individual contaminants in their specific conditions or locations at the site. The applicable technologies are then assembled into definable remedial alternatives that will address the combinations of contaminants and their locations to interrupt the linkages between the conceptual model elements shown on Figure 4-116. The selected remedial alternatives that have been identified are then evaluated in detail to compare their relative effectiveness in reducing or eliminating the risks posed by the site contaminants.

Target analytes in soil include Cr(VI), nitrate, arsenic, barium, total chromium, mercury, lead, carbon-14, cesium-137, cobalt-60, europium-152, nickel-63, plutonium-239, plutonium-240, strontium-90, uranium-238, uranium-234, tritium, other radionuclides, TCE, and total petroleum hydrocarbons. A complete list of target analytes is provided in Table 2-9. These analytes are evaluated in Chapters 5, 6, and 7 to determine if they pose a risk to HHE, based on concentrations and distribution.

Soil contaminants are found distributed over various portions of the thickness of the vadose zone, depending on the location of their initial release, the quantity of water or other liquid discharged with them, and their relative mobility in soil. Most of the metallic contaminants (for example, lead, arsenic, barium, mercury, cesium-137, and radioisotopes of cobalt, europium, nickel, plutonium, and uranium) are found near the points of historical release.

Contaminants that migrated to groundwater have developed into identified groundwater plumes. Cr(VI) is recognized as a principal COPC in groundwater at 100-D/H because of its mobility, widespread presence, and potential effect to HHE. Other COPCs include aluminum, nitrate, arsenic, barium, total chromium, mercury, nickel, lead, cesium-137, cobalt-60, europium-152, nickel-63, plutonium-239, plutonium-240, strontium-90, technetium-99, uranium-238, uranium-233, uranium-234, tritium, and other radionuclides (Table 2-11). The COPCs for groundwater are evaluated to determine if they pose a risk to HHE and should be evaluated in the FS. Nitrate concentrations in the unconfined aquifer underlying 100-D show stable trends and a declining trend at 100-H. Strontium-90 concentrations in the unconfined aquifer underlying 100-D are consistent with levels found previously in the same location, with little change. Underlying 100-H, strontium-90 concentrations in the unconfined aquifer fluctuate seasonally, but exhibit a stable plume size. Tritium concentrations in the unconfined aquifer are generally declining.

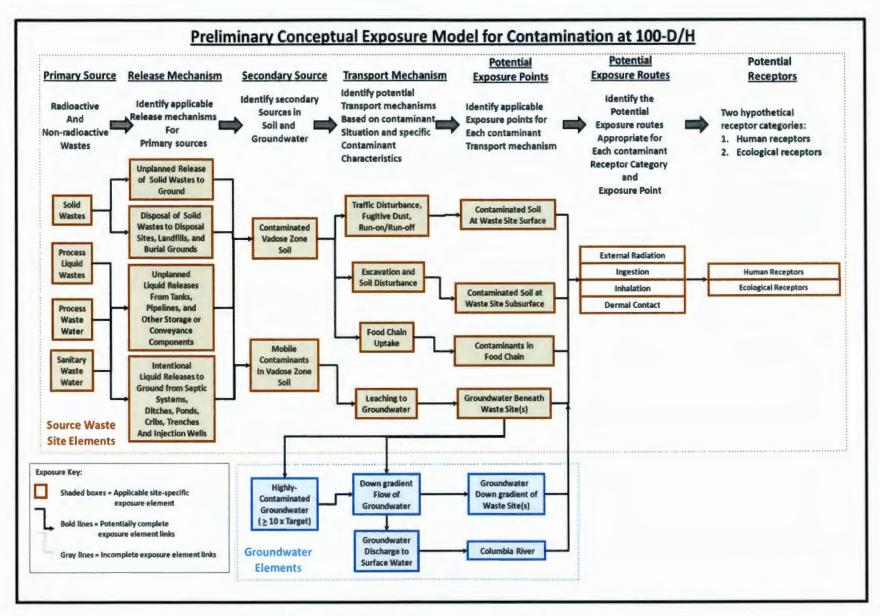


Figure 4-116. Preliminary Conceptual Exposure Model for Contamination at 100-D/H

### 4.9.3 Physical Environment of 100-D/H

The physical environment of 100-D/H is an arid to semiarid low-elevation habitat environment located in southeast Washington State adjacent to the Columbia River. The site was the location of established farming communities in the early part of the 20<sup>th</sup> Century and was selected for establishment of the Hanford Site for production of plutonium in 1943. The site receives 17.2 cm (6.8 in.) of mean annual precipitation and supports only a low-growing shrub-steppe plant community in upland areas. The native plants are adapted to use the available moisture by rooting sufficiently deep to take advantage of moisture stored over the winter in the upper few meters of soil. The infiltration rates used in the vadose zone models are selected from the upper end of available rates based on about 30 years of field measurements (lysimeter studies) and long-term isotopic recharge studies that necessarily incorporate the effects of the history of all land surface changes at the measurement sites, including past wild fires.

The Columbia River, which is flow-controlled by dam operations, is adjacent to 100-D/H and has long been used as a source of drinking and irrigation water. At the Hanford Site, the river was used during reactor operations as a source of cooling water. During development of the Hanford Site operations, the previously established farming operations were razed and the heavy industrial operations to support the reactor operations were constructed.

Construction activity in the reactor areas (which is less than one percent of the Hanford Site) resulted in removal of much of the vegetation and topsoil. Much of the surface was maintained as bare gravel, and weeds were strictly controlled. Without any native vegetation or topsoil, significant portions of the rainwater and snowmelt water could infiltrate the soil unabated.

The vadose zone in 100-D consists primarily of Hanford formation gravels with portions of Ringold Formation unit E sands and gravels near the water table. The gravel-dominated facies of the Hanford formation are typically well-stratified and contain little cementation, allowing for water to pass through the material more easily than through the more cemented Ringold Formation unit E. Lenses of black sand have been identified beneath 100-D that are finer-grained than typical Hanford formation gravel. These fine-grained sand lenses tend to reduce the vertical hydraulic conductivity of the vadose zone matrix. Underlying 100-H and the northern portion of the Horn, the vadose zone is dominated by the highly conductive, coarse-textured sand/gravel of the Hanford formation. These sediments are capable of draining significant amounts of water vertically, also allowing for faster horizontal water movement. Ground surface elevation in 100-D is about 143 m (470 ft) above mean sea level. The surface elevation drops to about 122 m (400 ft) above mean sea level in the central portion of the Horn, and is about 128 m (420 ft) near 100-H. The current depth to the water table beneath 100-D/H ranges from about 27 m (88 ft) bgs in the central portion of 100-D to 14 m (46 ft) bgs in central 100-H, and less than 5 m (16 ft) bgs near the Columbia River and in the northern portion of the Horn between the D and H Reactor areas.

The shallow unconfined aquifer is found within the Ringold unit E Formation beneath most of the 100-D operating area and within the Hanford formation at 100-H (Figure 3-8). In the intervening area of the Horn, the shallow unconfined aquifer is variably within the Ringold Formation unit E and Hanford formation. This difference in aquifer matrix contributes to a higher groundwater flow velocity beneath 100-H and in the northern portions of the Horn. During reactor operations, the water table at 100-D and the area of the Horn near 100-D, rose into the overlying Hanford formation in some locations.

The base of the unconfined aquifer is delineated by the surface of the RUM, and undulations in the RUM surface may also affect localized groundwater flow, especially where depressions exist (Figure 3-4). The upper part of the RUM sometimes contains gravel in a silt/clay matrix that may represent a transition zone (reworked interval) above the more massive silt or clay. Within the RUM, thin sand-to-gravel lenses form zones with variable hydraulic conductivities that range from low to high. Beneath a localized area of

100-H, the first water-bearing unit within the RUM has been shown to be hydraulically connected to the unconfined aquifer (see Section 3.7.4), and could provide a pathway for contaminants to migrate.

#### 4.9.4 Contamination Sources

Historical releases of various liquid and solid wastes were the primary sources that resulted in contamination of the vadose zone and underlying groundwater. Contamination migrated through the vadose zone to groundwater. In turn, the contaminated groundwater migrated downgradient into the Columbia River. The control of discharge of contaminants from groundwater into surface water is important to recognize as a key objective of remedial actions. Ongoing remedial actions at 100-D/H, such as the groundwater pump-and-treat systems, are actively reducing the potential for impacts to the river.

### 4.9.4.1 Primary Sources

The primary sources identified at 100-D/H consisted of low-volume, highly concentrated water treatment chemicals, widely variable volumes of liquid effluent discharged or released from various points in the reactor process, and solid waste. Releases took place during operations at the three 100-D/H reactors and during waste management operations that followed cessation of reactor operations in the early 1970s. The addition of contaminants to primary sources at 100-D/H ceased with the end of reactor operations. Figure 4-117 is an aerial view showing 100-D and 100-H during operations.





Figure 4-117. Aerial Photograph of D and H Reactors During Operations

Primary contaminant sources consisted of low-volume, highly concentrated sodium dichromate, widely variable volumes of liquid effluent discharged or released from various points in the reactor process, and solid waste. Specific primary sources of contaminants include the following:

- Episodic planned disposal of solid waste materials including chemical wastes, construction materials
  and debris, repair and maintenance wastes, and radiologically contaminated tools, materials, and
  reactor components (some highly radioactive and irradiated fuel fragments) placed in burial grounds.
- Episodic planned disposal and unplanned releases of liquid waste materials, including radiologically contaminated decontamination solutions associated with reactor repair and maintenance activities, off-specification or surplus water treatment chemicals, reactor cooling gas condensate, and FSB leakage. The conditioning processes added specified concentrations of chemicals, including alum, chlorine, sodium dichromate, and sulfuric acid. This category of primary source material includes spills, leaks, and wash-down of high-concentration sodium dichromate dihydrate stock solution and moderate-concentration sodium dichromate dihydrate working solution. The historical release of concentrated sodium dichromate dihydrate solution appears to account for persistent groundwater plumes near the 105-D and 105-DR Reactors water treatment facilities. Reactor cooling gas

condensate releases and spent nitric acid disposal at cribs adjacent to the reactors appear to account for persistent plumes of nitrate near the reactors. Only minor amounts of nitrate are observed at 100-H.

- Groundwater contaminant plumes beneath 100-D/H are mainly attributed to the primary source materials and a limited number of confirmed, or potential, release points. Before entering the 105-D, 105-DR, and 105-H reactors, cooling water was treated for corrosion control by adding sodium dichromate working solution to the water to achieve an operating sodium dichromate dihydrate concentration of 2,000 μg/L. The nearly continuous planned disposal, as well as the unplanned releases, of large volumes of this cooling water appears to have caused the extensive plume of Cr(VI) in the unconfined aquifer underlying the Horn area between 100-D and 100-H.
- Cr(VI) contamination has been observed in groundwater within the first water-bearing unit of the RUM in one well in the Horn and a localized area near the river at 100-H. Groundwater mounding resulting from reactor operations at 100-D is thought to be responsible for the Cr(VI) contamination in Well 699-97-48C, which is completed in the RUM and located in the Horn, but downgradient from the 116-DR-1&2 Trench. Groundwater mounding due to reactor operations at 100-H is thought to have caused the low Cr(VI) contamination in the first water bearing unit of the RUM in the 100-H area. The increased hydraulic head resulting from these groundwater mounds likely pushed contaminated cooling water into the uppermost water-bearing unit of the RUM at areas where the RUM material is more porous, and therefore more transmissive, or through erosion exposures. Contamination in this lower aquifer zone is a potential secondary source to the unconfined aquifer above where an upward gradient exists.
- Reactor cooling water was contaminated with short-lived activation products and, following reactor
  fuel cladding failures, with the entire suite of uranium and mixed fission and activation products
  present in the irradiated fuel. Releases of cooling water are responsible for most of the soil and
  groundwater contamination observed near the cooling water retention basins, trenches, and cribs.
- Historical septic systems and the disposal of nitric acid from reactor operations are believed to have caused or significantly contributed to the nitrate plume in the unconfined aquifer underlying 100-D and 100-H.
- Other chemical wastes generated and released at 100-D/H included the water treatment chemicals that were received, stored, and used in large volumes in the head house areas. These include strong mineral acid and caustic as well as toxic materials (for example, sodium dichromate dihydrate solution). Following the fuel cladding failure, highly radioactive liquid had to be removed from the reactor pile to recover operations. This liquid was discharged to the subsurface disposal structures.

Contaminants introduced into the environment included metals, radionuclides, and solvents (Tables 2-12 and 2-13). Soil contaminants are found distributed over various portions of the thickness of the vadose zone, depending on the location of their initial release, the quantity of water or other liquid discharged with them, and their relative mobility in soil. In some instances, contaminants that migrated to groundwater have developed into identified groundwater plumes. Cr(VI) is recognized as a COPC in soil and groundwater at 100-D/H because of its mobility, widespread presence, and potential effect to HHE. Analytes in soil and groundwater are evaluated in Chapters 5, 6, and 7 to determine if they pose a risk to HHE, based on concentrations and distribution, and should be further evaluated in the FS.

Previous actions undertaken under interim action RODs and CERCLA removal actions have addressed the environmental threats posed by majority of primary sources. Remedial actions will address any remaining primary sources but the focus is on control of contamination associated with secondary sources that may result in either direct contact exposure to identified receptors, or be released and transported to groundwater or surface water, where potential exposures may occur.

### 4.9.4.2 Low-Concentration/ High-Volume Waste Sites

Total chromium and Cr(VI), as well as mixed fission products, are key contaminants for this type of waste site, which includes retention basins and selected trenches such as the 116-DR-1&2 Trench and 116-H-1 Trench. These contaminants are primarily associated with cooling water, which made up the greatest percentage of the low-concentration/high-volume wastes, with process sewers being a secondary contributor.

Chronic leaks in the conveyance system piping, retention basins, and infiltration from trenches were sufficient to create substantial groundwater mounds beneath the reactor areas. The most dramatic effects of planned liquid releases occurred in 1967, when the entire cooling water waste stream from the 105-D Reactor was discharged directly to the ground via the 116-DR-1&2 Trench, resulting in a substantial temporary increase in the magnitude of the 100-D groundwater mound present under normal operating conditions. As a result of normal operations combined with the effect of the 1967 infiltration test, the contaminated cooling water from 100-D spread over an area of about 16.6 km² (6.4 mi²). The affected area includes the developed industrial portions of 100-D and 100-H areas (about 2.8 and 1.8 km² [1.0 and 0.7 mi²], respectively), and about 12 km² (4.6 mi²) of the Horn, located between the two reactor sites.

As these large fluxes of coolant water with a low concentration of Cr(VI) passed through the saturated vadose zone and aquifer matrix, a small fraction would tend to reduce and become immobile. In the presence of acidic conditions and where the ferrous ion is available, the +6 oxidation state of chromium will reduce to its +3, or trivalent, state, which is both less mobile and less toxic. Where the ferrous ion is present with sulfide, this process will take place in both neutral and alkaline conditions. The reduction process would be expected to continue over time, lacquering a small fraction of the total flux onto the sediment, resulting in relatively large concentrations of Cr(III) in sediments associated with these low-concentration/high-volume sites.

After operations ceased, the large groundwater mound beneath 100-D that extended out across the Horn, and the comparatively smaller mound below the retention basin at 100-H both collapsed as water drained down to the water table. As the groundwater mound receded, it left relatively normal groundwater levels formed by the newly emplaced cooling water. In areas of the Horn near 100-D, where the groundwater mound was the highest, contaminants present in the groundwater with low to moderate  $K_d$  values could have been "stranded" in the deeper areas of vadose zone as this mound collapsed. These less mobile contaminants would remain available for downward migration to the water table, if a driving force such as water were present in sufficient amounts. Remnants of cooling water would potentially be present in the vadose zone in a volume roughly equal to the specific retention (porosity minus specific yield) or field capacity. This is approximately 2-5 percent of the total volume, depending on the sediment composition (sand versus silt versus gravel).

Key aspects of contaminant migration from low-concentration/high-volume waste sites include the following:

- Very large volumes of contaminated cooling water containing relatively low concentrations of Cr(VI) and radionuclides were discharged. Although the Cr(VI) concentration of the cooling water was low relative to the highly concentrated feed stock, the residual Cr(VI) plume across the Horn still exceeds the cleanup target concentration over a large area (Table 4-19).
- A small fraction of the daily Cr(VI) flux would be reduced to Cr(III) under reducing conditions as it
  passed through the sediment, dropping out of solution and building up in the vadose zone and aquifer

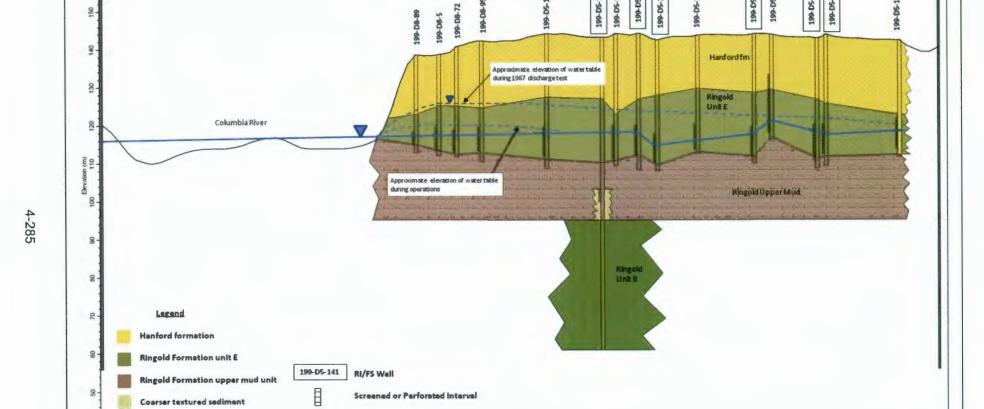
matrix. This is evident where there are large total chromium concentrations remaining relative to the remaining Cr(VI) concentrations.

- Cooling water effluent moved vertically through the vadose zone, and flowed laterally in the
  unconfined aquifer. These high-volume discharges created a transient water table mound beneath the
  reactor operating areas. Distribution of contaminants inland also occurred because of the mounding.
- Mounded cooling water effluent entered the first water-bearing unit in the RUM in a localized area underlying the 105-H Reactor, where the RUM thins and there is a hydraulic connection between this unit and the overlying unconfined aquifer.
- Groundwater movement follows the path of least resistance, taking with it the contamination from the cooling water. During operations, the elevated water table at 100-D rose to a level of approximately 125 m (410 ft) amsl (Status of the Ground Water Beneath Hanford Reactor Areas January, 1962 to January, 1963 [HW-77170]). The plan view map of the cross section is presented in Figure 4-91. At this elevation, the water table extended into the Hanford formation, above the Ringold Formation unit E at 100-D in some locations. Figure 4-118 shows a cross section to the west of the highest groundwater elevations and even in that location, the water table shows a significant elevation change. In 1967, during the infiltration test, the water table rose to over 126.5 m (415 ft) amsl (Ground Disposal of Reactor Coolant Effluent [BNWL-CC-1352]), well into the Hanford formation at some locations.
- The large groundwater mound at 100-D migrated across the Horn, tending to move within the Hanford formation material instead of back into tighter sediments of the Ringold Formation unit E. However, where Ringold Formation unit E was present, the elevated water table would have likely remained above the Ringold to Hanford contact, allowing for contamination in those areas. Figure 4-119 presents a conceptual graphical depiction of flow from the waste sites through the aguifer matrix at variable flow velocities.
- Contaminants were transported through the vadose zone or unconfined aquifer according to their
  relative mobility. Highly mobile constituents, such as Cr(VI) and tritium, migrated with groundwater,
  while less mobile constituents such as strontium-90 migrated more slowly through the vadose zone
  and aquifer system.

### 4.9.4.3 High-Concentration/Low-Volume Waste Sites

The high-concentration/low-volume waste sites were liquid and solid waste disposal sites and surface spills. The routine discharges tended to be episodic and related to specific operation or maintenance functions (for example, reactor refueling, decontamination, repair activities, and deionization system regeneration). Additional release mechanisms include leaks of concentrated solutions from storage locations and conveyance systems, as well as discharges to cribs and French drains. These waste sites are significant because of high concentrations of contaminants such as Cr(VI) in the sodium dichromate feed stock.

At the 105-D, 105-DR, and 105-H Reactors, the sodium dichromate stock solution was generated and managed in several ways over the life of the reactors. Initially, sodium dichromate was procured as a crystalline solid at a purity grade of greater than 99 percent. The solid sodium dichromate was dissolved in water to make a 70 wt% solution. The 70 wt% solution was subsequently diluted to a 15 wt% working solution, which was then pumped through pipelines to the cooling water head houses and metered directly into the reactor cooling water to achieve the final cooling water concentration of about 2,000  $\mu$ g/L Cr(VI).



100-D/H Area Geologic Cross-Section B-B'

199-DS-132

199-D5-133 199-D5-129

Vertical Exaggeration = 10X

2000

1900

1700

CHPUBS\_100DH\_0181

2100

170

Ringold Formation unit 8

Figure 4-118. Estimated Groundwater Elevations During Operations and 1967 Infiltration Test at Cross Section B to B'

1200

1300

**Total Depth Drilled** 

500

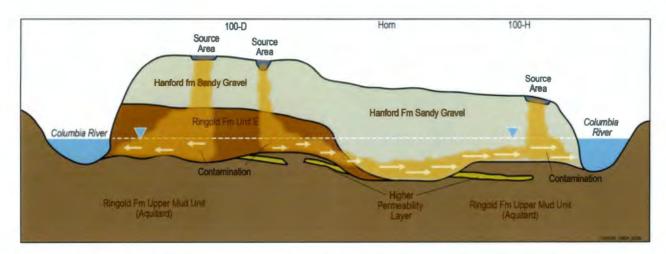


Figure 4-119. Conceptual Representation of Contaminant Flow Through Aguifer Material

The highly concentrated stock solution was released to the environment through spills and washout of vehicles and containers and also through leaks in the conveyance system. These releases, most of which occurred at or near the ground surface, resulted in gross contamination of the vadose zone at many locations within 100-D/H. This includes the 100-D-100 waste site, which coincides with the 105-DR reactor sodium dichromate pipeline (100-D-56 waste site) as well as the railcar solution transfer station. The historical releases may account for potential areas of residual contamination in the vadose zone in this area. Similar conditions have been observed at the 105-H Reactor but at a much lower magnitude of contamination. Key aspects of high-concentration/low-volume waste sites (many of which have been remediated under interim actions) and migration of contaminants associated with them include the following:

- Initially, dry sodium dichromate was used to prepare feedstock at the 108-D Building Chemical Pump House. The concentrated solution was pumped to tanks in the 105-D and 185-D Buildings. This preparation process was relocated in 1950 to the 185-D De-aeration Plant. Two piping lines (100-D-56) were installed between the 185-D De-aeration Plant and the 183-DR Head House for the transfer of the feedstock. Spills during product handling and leaks from piping have contributed to Cr(VI) contamination near the 183-DR Head House. Dry sodium dichromate was also used at 100-H (1949 to 1959), with a similar process as that conducted at 100-D.
- High-concentration sodium dichromate (70 wt% solution) was received at the railcar unloading site and transferred into storage tanks near the 190-D and 190-H Building (Section 1.2.2). Complete transfer of these railcar or tanker fluids into the pumping facility did not occur. Residuals were drained from the transfer hoses between the pumping station and railcars and tankers. These residuals and rinse water were discharged directly into a nearby French drain about 0.9 m (3 ft) in diameter. This was an important primary source for the present-day high-concentration Cr(VI) plumes near the 105-D and 105-DR Reactors. There is presently not a high-concentration Cr(VI) plume near the 105-H Reactor.
- The other important source for sodium dichromate concentrated solution is leakage from the pipelines
  that transferred the concentrated solution to the head houses upstream from the reactors, where it was
  input to the cooling water stream.
- Some of the high-concentration solutions may have been the result of cleaning operations at the 108-D Building Chemical Pump House where rinse water was discharged to the process sewer. The process sewer discharged directly into the Columbia River and later to the 116-DR-1&2 Trench.

One likely scenario is that at the end of operations, concentrated solution was cleaned out via the process sewer, ending up in the 116-DR-1&2 Trench. Therefore, discharges to the 116-DR-1&2 Trench may have been both low-concentration (cooling water) and high-concentration solutions.

- Sulfuric acid was used at 100-D/H primarily as a decontamination solution, with some used in water treatment. Mercury-contaminated commercial-grade sulfuric acid was used for cooling water pH adjustment at 100-K (1968 to 1977) and it is possible that mercury contaminated acid was also used 100-D and 100-H. Although this period was after the shutdown of the 100-D/H reactors, mercury contamination in soil associated with sulfuric acid has been identified during the remediation of the 100-D-77 waste site at the 183-DR Head House and at 100-H-44, near the 183-H Head House. Since other locations with acid staining that did not have mercury have also been identified, however, it is not a certainty that the acid was cross-contaminated.
- 100-H historically exhibited some mercury contamination in groundwater, apparently related to the
  use of the 183-H Settling Basins as a solar evaporation pond for chemical waste following cessation
  of reactor operations. In addition, mercury contamination of sulfuric acid has been identified at the
  183-DR Head House and may be associated with the 183-H Head House.
- The 100-D/H nitrate groundwater plumes originate near each reactor and the sources are likely related to reactor operations. The likely source of nitrate may include historical use of nitric acid-based solvents in the reactor buildings, including laboratory areas, as a decontamination solution. Another reactor operation-related source is from oxidation of ammonia discharged in the condensate solution. Some additional contribution from septic sources is possible. Detailed analysis of the vadose zone profile at 1607-H-4 in the RI did not find nitrate above background (52 mg/kg).
- Elevated sulfate in groundwater at 100-D/H has originated from multiple sources. Sulfuric acid was
  primarily used at 100-D/H as a decontamination solution, with some possibly used to adjust cooling
  water pH. Sulfuric acid was also used to produce alum from bauxite ore to be used in cooling water
  treatment. The highest sulfate concentrations currently are found near the ISRM barrier at 100-D near
  100-DR Reactor and result from the oxidation of the sodium dithionite reductant used to establish that
  reactive treatment zone.

**Special Case: 183-H Solar Evaporation Basins.** In addition to the typical high concentration liquids used at the reactors, different types of liquid waste were managed at the 183-H Solar Evaporation Sedimentation Basins. The basins were originally used as part of the water treatment facility (1943 to 1964). After cessation of operations at the 105-H Reactor (1973), the basins were converted for use as solar evaporators Neutralized nitric and sulfuric acid wastes, generated by reactor fuel fabrication processes in the 300 Area, were transferred to the open-topped basins and allowed to evaporate.

During their use as evaporation basins, one of the basins apparently leaked waste contents to the underlying vadose zone. Nitrate contamination in Well 199-H4-3 was attributed to seepage of wastes from the unlined basin #1 in 1978. As a result, basin #1 was removed from service but sludge material was left in place. The remaining basins were coated/ lined prior to use (*Geohydrologic Characterization of the Area Surrounding the 183-H Solar Evaporation Basins* [PNL-6728]).

The primary wastes discharged to the 183-H Basins were acid solutions (HN0<sub>3</sub>, H<sub>2</sub>S0<sub>4</sub>, HF, and H<sub>2</sub>CrO<sub>4</sub>) neutralized with sodium hydroxide (NaOH). Small quantities of other chemical wastes were also discharged to the 183-H Basins on a non-routine basis.

The main contaminants in groundwater associated with the 183-H Solar Evaporation Basin are Cr(VI) and nitrate. Nitrate and Cr(VI) concentrations appear to fluctuate seasonally, with concentrations typically

rising when groundwater elevations are low in most of the wells downgradient from the basins. In Well 199-H4-84, located in the basins, concentrations rise during high water periods.

Uranium has also been detected in groundwater downgradient of the basins on a periodic basis, and the waste site was not fully excavated to groundwater. Based on the nature of the waste that was treated and the somewhat elevated activities in the upper interval of the pre-soil remediation boreholes, uranium appears to be present in soil just above groundwater.

Groundwater monitoring data show a fluctuation in uranium concentrations that appear to be related to water table changes. The data indicate that the mass remaining in the rewetted zone is remobilized when the water table rises, and the mass is being depleted over time as shown by the downward trend in concentrations resulting in current concentrations below the DWS.

### 4.9.5 Secondary Sources

Secondary sources are the environmental media (for example, soil, surface water, and groundwater) that were affected by the initial releases of primary sources and, subsequently, retained sufficient levels of mobile contamination to function as continuing sources of contamination to adjacent soil, surface water, groundwater, and/or air.

The historical releases of primary contaminant source material to the environment resulted in contaminated vadose zone material beneath facilities and waste sites and contaminated groundwater. The resulting contamination, with varying mobility, is subject to leaching to groundwater, to transport by surface run-on or run-off, and/or to transport by wind as particulates. Surface run-off and wind are not considered important pathways contributing to current contamination levels (see Appendix K). If not remediated, this contaminated material acts as a secondary source with potential for the further spread of contaminants through the environment and potential exposure to human and ecological receptors. The main secondary source of concern at 100-D/H is vadose zone soil, including the PRZ, and possibly in low-conductivity zones of the unconfined aquifer. While Cr(VI) is the main secondary source of concern, other COPCs also may be present in these zones.

Chapters 6 and 7 discuss the evaluation of risks posed by the identified secondary sources to human health and the environment, respectively, through direct exposure. The potential for secondary sources to provide a significant ongoing source of contamination to groundwater is evaluated through the comparison of contaminant EPCs in vadose zone materials to the SSLs and PRGs (Section 5.6) protective of groundwater and surface water.

Waste remediation has been oriented toward removal of secondary sources of contamination at waste sites (Section 1.2.2). Confirmation sampling and RI characterization data (Section 4.3) indicates that cleanup goals have been achieved within the vadose zone; however, groundwater monitoring indicates that the potential for residual contamination in soil exists. During high river stage, groundwater rises into contaminated vadose zone materials, increasing the rate at which contaminants are leached to the groundwater and causing a temporary peak in concentrations. Contaminants with higher K<sub>d</sub> values would also tend to leach, but at significantly lower rates, as discussed in Chapter 5.

Based on the historical and current presence of specific groundwater plumes in 100-D/H, the following general locations are potential areas of residual contamination in the vadose zone that may contribute to groundwater contamination:

• Groundwater monitoring around the 105-D and 105-DR reactors indicates potential for residual contamination in these areas.

- The FSB leaks, disposal cribs, and trenches were historical sources of Cr(VI) and mixed fission product (i.e., strontium-90, tritium, and cesium-137) contamination. Strontium-90 and Cr(VI) groundwater contamination remains in these areas and indicates potential for residual contamination in the vadose zone.
- Groundwater monitoring around the high concentration sodium dichromate off-loading, mixing, and delivery system.
  - Chromium contaminated vadose zone soil underlying the sodium dichromate dihydrate solution transfer facilities are potential areas of residual Cr(VI) contamination. These areas include the vicinity of the 100-D-100 waste site and other related conveyance systems.
- High volume/low concentration cooling water disposal areas are potential areas of residual contamination contributing to groundwater.
  - Various cribs and trenches (such as 116-D-1A, 116-D-1B, and 116-D-4) received low concentration, high volumes of contaminated cooling water. Other associated waste site areas include the 116-DR-1&2 Trench and the 116-D-7 and 116-DR-9 retention basins.
  - Groundwater beneath the footprint of the 116-DR-1&2 Trenches, associated with the former groundwater mound, likely accounts for most, if not all, of the residual groundwater Cr(VI) across the Horn. The collapse of the groundwater mound likely resulted in contaminants remaining in the vadose zone, which may serve as a residual source to groundwater.
  - Areas at 100-H that were historical sources of Cr(VI) include the 116-H-7 retention basin and various cribs and trenches. Monitoring in these areas has not indicated the presence of residual contamination.
- The 183-H solar evaporation basin (116-H-7) area contains residual contamination in the vadose zone.

No areas of high concentration Cr(VI) contamination are observed in the unconfined aquifer beneath 100-H. This indicates that the significant secondary sources, areas that received high concentration stock solutions or where spills may have occurred, have been remediated and residual contamination is not present.

In addition, the interim action pump-and-treat remedy made significant progress at 100-H in cleaning up Cr(VI) derived from the 105-H Reactor in the unconfined aquifer. Additional small areas of this contamination remain and additional Cr(VI) is migrating in groundwater from the Horn area into 100-H.

#### 4.9.6 Release Mechanisms

Primary release mechanisms are the processes during operations that resulted in the initial distribution of contaminants to the environment. Secondary release mechanisms are the processes that result in the redistribution of secondary source contaminants to other environmental media.

# 4.9.6.1 Primary Liquid Waste Release Mechanisms

The primary release mechanisms of liquid wastes at 100-D/H fall into two general categories: intentional or planned releases and unplanned releases. As discussed previously, the two groups of liquid wastes are high-volume/low-concentration liquids and low-volume/high-concentration liquids. These types of discharges were directly related to reactor operations, with discharges generally being released to various cribs, trenches, retention basins, and other engineered structures. Occasionally, planned releases allowed for discharge directly to the ground surface. For example, contaminated reactor cooling water during

upset conditions, reactor cooling gas condensate, and captured FSB leakage were released directly to the land surface and allowed to infiltrate. Other planned releases at 100-D/H that appear to have made substantial effects on vadose soil and groundwater include releases to numerous French drains, cribs, and trenches.

Unplanned releases were primarily from leaks of the retention basins, but also included releases from tanks, spills, and leaks from conveyance systems. Liquid wastes were also released from pipelines through leaks at joints or material failure between joints as a result of corrosion or other damage.

The timing aspects of the liquid source releases range from episodic, short-term releases (for example, spills or transfer leaks at the head house storage areas) to regular periodic releases (for example, gas dryer condensate releases, fuel storage basin overflows, and sedimentation basin flushes) and near-continuous discharges of spent reactor cooling water.

# 4.9.6.2 Primary Dry Waste Release Mechanisms

Contaminants associated with dry solid waste were released to the environment through intentional disposal at waste sites or through unplanned releases of particulate material. The contaminants may transfer to the environment through leaching or dissolution. Dry granular or crystalline chemical products or contaminated soil particulates may also become windborne, suspended in surface run-off, or transferred to the surface through physical contact with a contaminated surface. These releases were evaluated during that waste site discovery process and data indicate that airborne contaminants are not significant (Appendix K). Intentional/planned releases of solid waste are believed to account for the large majority of historical dry waste releases to the environment. Dry contaminants also include powdered Cr(VI) that may have been spilled during operations and was subsequently either swept up or washed down.

Solid wastes were typically disposed through burial in landfills and burial grounds as a planned release. Unplanned releases of solid wastes included spills of dry sodium dichromate or other solid chemicals. Waste site remediation is ongoing and is removing these types of wastes.

#### 4.9.6.3 Secondary Source Release Mechanisms

Contaminated material that remains in the environment is considered a potential ongoing secondary source of some contaminants released to air, groundwater, surface water, or to the riparian zone. Secondary sources remaining in pipelines and control structures in the form of pipe scale, corrosion products, sludge, and sediment may be released through structural failure of the pipeline and exposed to net infiltration. The following secondary release mechanisms for contaminants are grouped by importance, with some being present as both historical and current mechanisms:

Historical release mechanisms with a minor contribution to the environment:

- Volatilization of contaminants in near-surface soil to the atmosphere or soil gas (applicable to VOCs and tritium)
- Transport of contaminants from surface soil in surface water run-off, both as dissolved constituents and suspended particles (applicable to all contaminants)

Historical release mechanisms with more significant potential to affect the environment:

- Desorption and/or dissolution from contaminated vadose zone soil and transport with infiltrating precipitation or other water sources (applicable to soluble and mobile contaminants)
- Direct release of reactor process-related chemicals

Current release mechanisms with minor potential to effect the environment:

- Resuspension of particulates in air (applicable to all contaminants) from contaminants at the soil surface
- Transport of contaminants from surface soil in surface water run-off, both as dissolved constituents and suspended particles (applicable to all contaminants)
- Biotic uptake (applicable to soluble and mobile contaminants located in the shallow vadose and riparian zone) and translocation in plants and animals

Current release mechanisms with more significant potential to effect the environment:

- Desorption and/or dissolution from contaminated vadose zone soil and transport with infiltrating precipitation or other water sources (applicable to soluble and mobile contaminants)
- Groundwater discharge to surface water and to the riparian ground surface when contaminated groundwater discharges in seeps and springs associated with seasonal high river stages (applicable to soluble contaminants contained in groundwater)
- Groundwater discharge to surface water through upwelling into the river
- Contaminants with a high K<sub>d</sub> held within the PRZ, which may be released by dissolution, ion exchange, or advective flow when groundwater elevations periodically re-enter this zone
- Desorption and/or dissolution from contaminated soil within the saturated material below the water table as a result of groundwater fluctuations and flow

### 4.9.7 Transport Mechanisms

The driving forces of contamination are either artificial or natural. The artificial forces during operations were related to the reactor operations and waste disposal practices, including the large groundwater mound at 100-D and the smaller mound at 100-H. The practice of disposing high volumes of liquid waste has contaminated the vadose zone and groundwater. Maintaining safe work conditions during remediation by applying water to control dust is postulated to have been a transient driving force. However, the long-term driving force is the natural system, as described by the hydrologic cycle.

The hydrologic cycle plays an important role in the CSM. Most of the precipitation occurs during the fall and winter months, when evaporation and plant use are the lowest. This water is stored in the upper few meters of the soil column and is available for plants during the dry summer months. A small fraction of water may percolate below the root zone, where it will continue to drain essentially undisturbed vertically through the vadose zone to the water table.

At 100-D/H, the groundwater currently flows toward the Columbia River, which forms the discharge boundary for the shallow unconfined aquifer. The transition area between the aquifer and the river is called the hyporheic zone. The Columbia River is free-flowing through 100-D/H and river stage, which can vary as much as 3 m (10 ft), and is controlled by the Priest Rapids Dam. When the river rises, the river water pushes into the riverbank, pushing back on the aquifer and causing the water table to rise in the nearby aquifer. When the river stage drops, groundwater in the aquifer flows again into the river.

In addition to discharge of groundwater to the river through the hyporheic zone, groundwater seasonally discharges in springs or seeps at elevations above the river stage. This occurs generally during the period following seasonal high river stage in the early summer. As the river stage recedes after the spring thaw,

groundwater that has become elevated as it equilibrated with the high river stage may drain directly to the ground surface in the riparian zone.

## 4.9.8 Contaminant Migration

Contaminants migrate along flow paths. Understanding of the flow path for contaminant migration is important in the development of the remedial alternatives in Chapters 8 and 9. The goal of a remedial alternative or combination of alternatives is to break the flow path and isolate or remove the contaminant. The major components of the flow path are illustrated on Figure 4-120. The upland zone to the right in the figure is the location of the reactors and facilities and associated waste sites. Once contaminants entered the ground through leaks at basins or pipes, planned releases at cribs and trenches, and other unplanned releases, the contaminant fluids combine with the ambient water already in the vadose zone soil plus precipitation and begin to leach down toward the water table.

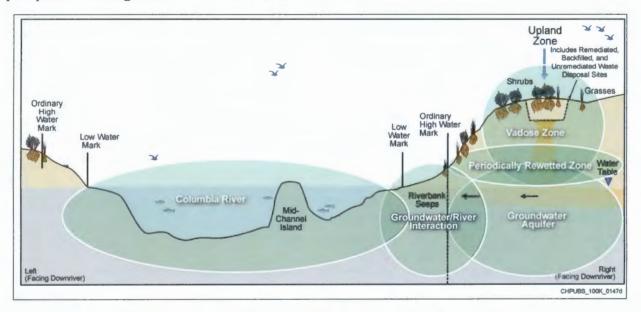


Figure 4-120. Schematic of Areas of Contaminant Interaction with Vadose Zone Soil, Groundwater, and Surface Water

Contaminants are distributed across the thickness of the vadose zone at 100-D/H. The extent of their distribution depends on site-specific factors, including: their initial release location, the quantity of water (or other liquids) discharged with them, the initial concentrations and volumes discharged, and their relative mobility in the soil. Source remediation removes the engineered structure and soil contaminants as necessary to reduce or eliminate the potential for direct exposure migration through the vadose zone to the groundwater, and wind-blown suspended particles. This has included remediation extending deep into the vadose zone, and as far as the unconfined aquifer for several 100-D/H waste sites to remove deep vadose zone Cr(VI) and other contamination and protect groundwater and the river. As stated in Section 4.9.8.1, less mobile constituents, such as strontium-90, would tend to bind to the soil particles in the upper vadose zone and be more easily remediated prior to impacting groundwater.

Contaminants in 100-D/H include highly mobile constituents that do not adsorb readily to the geologic materials in either the vadose zone or the aquifer. These contaminants include Cr(VI), nitrate, sulfate, and tritium, which migrate readily with water. Strontium-90 has been found in the deep vadose zone and in groundwater, but tends to adsorb readily to the geologic materials in the vadose zone and aquifer and does not move much further under natural conditions. In the presence of acids, strontium-90 and other metals

would be more mobile, but the buffering capacity of the sediment would neutralize the leachate and reverse the process.

Where mobile contaminants remain in the vadose zone, precipitation or other water sources have the potential to mobilize those contaminants. Although there is no evidence that residual wastewater from operations is still present to act as a driving force, both precipitation and dust suppression water may contribute to water infiltrating through the vadose zone. As seen during interim remedial action activities, such as at waste sites 100-D-100, 100-D-30, and 100-D-104, highly mobile contaminants such as Cr(VI) can be left in place throughout the vadose zone from near the surface to the water table, unless mobilized. As contaminants are driven down through the vadose zone, which is about 26 m (85 ft) thick in 100-D, they would do so in pulses associated with the presence of water, the driving force. The concentrations of residual contaminants at remediated sites, potential secondary sources, were evaluated in their respective CVP reports and reported to be below the applicable cleanup criteria.

Residual contaminants that remain in the vadose zone after the cessation of waste discharges can migrate downward by any of four mechanisms:

- They may continue to move by gravity drainage of residual wastewater within the vadose zone (this
  process is not believed to be continuing at this time).
- They may be mobilized in the fraction of annual precipitation that actually percolates deep into the vadose zone to recharge into the aquifer.
- They may be mobilized into groundwater from the vadose zone during seasonal increases in groundwater table elevation resulting from high river stages.
- They may be mobilized in water added for dust control during remedial actions (for example, excavation) and migrate deeper into the vadose zone.

Other factors that affect contaminant migration include persistence and chemical changes, including radioactivity. These factors relate directly to the way the individual constituent reacts in the environment.

The persistence of various contaminants determines how long they are available to the environment and for transport to the different receptors. If a contaminant remains in the environment for a long time, and is highly mobile, it is more likely to be transported from the vadose zone to the groundwater, and eventually to the surface water. Persistence is defined by how long it takes a particular contaminant to be transformed into a less toxic or less available form, or how long it takes the contaminant physically to leave the affected area. Radionuclides undergo radioactive decay at varying rates specific to the individual nuclide. Chemicals may also degrade, decay, or undergo chemical transformation that reduces the residual mass of the contaminant available for transport or direct exposure.

**General Chemical Changes.** Several constituents also may be altered into a different valence state as a result of the chemistry of the water or lithologic composition of sediments in which they are present, resulting in a change to the mobility. For example, Cr(III) adsorbs and precipitates out of solution and becomes immobile. The chemistry of sodium dichromate is important for this reason.

The geochemistry of sodium dichromate is important. Chromium is typically present in the environment in one of two oxidation states (chromium(III) or Cr(VI)). When chromium is in the hexavalent state (with a +6 valence), the chemical form is present as a soluble oxyanion, either as the dichromate anion ( $Cr_2O_7^{2-}$ ) or chromate anion ( $CrO_4^{2-}$ ), depending primarily on pH. The dichromate anion is dominant in acidic conditions and the chromate anion is dominant in alkaline conditions. Chromium(III) is typically precipitated as a low-solubility hydroxide molecule,  $Cr(OH)_3$ , and has low mobility. Most soil types,

including those found at the Hanford Site, tend to be negatively charged as well, so there is no significant force of attraction between the chromium anions and the sediment, such that typically the adsorption is assumed to be very low for dichromate passing through the sediment. However, at locations where iron and bacteria are available to react chemically and biologically with the dichromate anion, reaction occurs and immobile chromium(III) forms can precipitate out of solution. Chapter 5 discusses in detail the fate and transport for contaminants in 100-D/H.

The ionic forms of Cr(VI) are relatively stable at the oxidation state typically found in soil and groundwater at 100-D/H and the constituent tends to remain mobile. The source of the Cr(VI) in the environment was the sodium dichromate used for corrosion control in reactor cooling water. This compound is acidic in its concentrated form. However, the dichromate, or chromate, ion can react with other metals in the environment to form compounds of lesser solubility. These compounds can include potassium dichromate (which is about one tenth as soluble as sodium dichromate) and lead chromate (which is essentially insoluble in water). The Cr(VI) ions can also be subject to chemical reduction under moderately reducing conditions, or upon reaction with reducing agents such as ferrous iron. This reduction appears to be the case in both soil and groundwater. Ferrous iron is very effective at reducing Cr(VI) to Cr(III), producing a very low-solubility hydroxide molecule.

In groundwater, where iron, hydrogen sulfide, and bacteria are available to react chemically and biologically with the dichromate anion, reaction occurs and immobile Cr(III) forms can precipitate out of solution. Ongoing research by Lawrence Berkley National Laboratory, PNNL, and the University of Oklahoma as a joint project on reduction of Cr(VI) by microbial communities indicates that three different bacteria are present at 100-H that are capable anoxic reduction of Cr(VI) (*Microbial Community Changes During Sustained Cr(VI) Reduction at the 100H Site in Hanford, WA* [Chakraborty et al., 2010]). Other research ("Enhanced Microbial Reduction of Cr(VI) and U(VI) by Different Natural Organic Matter Fractions" [Baohua and Chen, 2003]) indicates that the presence of microbial activity for reduction of metals is also dependent on the pH and humic acid present. Section 5.6, Contaminant Persistence, discusses chemical reduction of chromium in more detail. Section 4.5.12, Secondary Groundwater Effects of the ISRM and In-Situ Treatability Testing, discusses the effects of creating a reducing environment within the groundwater.

**Radionuclide Decay.** The primary radionuclides associated with reactor operations that resulted in vadose zone and/or groundwater concerns at 100-D/H are strontium-90 and tritium. The half-lives of these radionuclides are presented in Table 4-31.

Analyte	Half-Life*	
Strontium-90	28.79 years	
Tritium	12.32 years	

Table 4-31. Half-Lives of Select Radionuclides

## 4.9.8.1 Vadose Zone

Historical contaminant migration at 100-D/H was driven by the release of large volumes of reactor cooling water to the ground surface, along with natural forces. With the cessation of operations, most discharges and releases ceased. However, contamination may continue to migrate under the influence of the hydrologic cycle and continue to interact chemically with the sediment matrix. The following are key features of the fate and transport:

<sup>\*</sup> Half-lives were obtained from the Radiochemistry Society (RS, 2011) website in February 2012.

- Waste site remediation has focused on reducing risk posed by direct contact exposures and achieving groundwater and surface water protection. These actions frequently included excavation of contaminated soil to remove contaminants that may pose a threat to groundwater. Although direct contact exposures are generally assessed within the upper 4.6 m (15 ft) of the vadose zone, the interim remedial actions were implemented to achieve defined RAGs and were not constrained to a specified depth of remediation (may have been shallower or deeper than 4.6 m [15 ft]). Sources contributing the majority of water to the surface during operations were related to reactor operations and waste disposal practices, including the release of varying quantities of wastewater to the vadose zone. Large quantities of contaminated cooling water were discharged to the ground at both 100-D and 100-H areas during reactor operations. Precipitation, dust suppression, and leakage from the FSBs and retention basins became the driving forces for contaminant movement through the vadose zone. Net infiltration from precipitation (recharge) on the nonvegetated surface soil would have been about 17 mm/yr (0.67 in./yr). Dust-suppression water was used during demolition and remediation of waste sites; this may have produced local recharge transient events. Once waste sites are revegetated, the plants transpire most of the natural precipitation, limiting infiltration deep into the vadose zone. Revegetation of waste sites at 100-D/H is variable and is expected to accelerate after completion of remedial activities.
- Some of the contaminants may remain dissolved in the pore water of the vadose zone material, but
  the mass in this phase is likely to be low (given the relative small volume of water) and slowly
  leachable (because it is located in smaller pores).
- Known chemical reactions within the vadose zone can reduce Cr(VI) to its less toxic and less mobile trivalent state in conjunction with sorption and precipitation ("Factors Affecting Chemical and Biological Reduction of Hexavalent Chromium in Soil (Losi et al., 1994). Chromium reduction by ferrous iron and chemical precipitation with barium sulfate are two reactions that occur; iron constitutes approximately five percent of the composition of both the Ringold Formation unit E and the Hanford formation.
- Chemical analysis of the vadose zone material at RI wells indicates that much of the chromium in the
  vadose zone is in reduced form. This is consistent with known attenuation mechanisms for Cr(VI)
  described by Monitored Natural Attenuation of Inorganic Contaminants in Ground Water Volume 2 –
  Assessment for Non-Radionuclides Including Arsenic, Cadmium, Chromium, Copper, Lead, Nickel,
  Nitrate, Perchlorate, and Selenium (EPA/600/R-07/140).
- Cr(VI) was discharged into the surrounding environment as a dissolved ionic species in various liquids. The historical records information described in a previous section shows Cr(VI) was released into the environment primarily as dissolved sodium dichromate dihydrate in two types of solutions: the low concentration reactor coolant and the high concentration 70 weight percent stock solution used to make reactor coolant. The differences in solution chemistry, associated production facilities, and discharge locations have had a substantial effect on current Cr(VI) distribution in the subsurface.
- With regard to ultimate Cr(VI) distribution in the environment, the significant solution properties are Cr(VI) concentration, pH, and specific density. The approximate Cr(VI) concentration was 466 g/L in the 70 percent by weight solution. This solution was acidic (pH about 1.5) and significantly more dense than water (specific gravity of 1.7 g/cm<sup>3</sup>). The main aquifer contamination from this stock solution appears to have originated near 100-D-100, 100-D-102, and 100-D-104.
- As described in Chapter 1, sodium dichromate dihydrate solid (Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-2H<sub>2</sub>O) and 70 wt% sodium dichromate-water solutions were delivered to 100-D/H. The dry material was received in bags and/or

drums at 100-D from 1944 until 1959, using the 108-D Building until 1950, and then the 185-D Building. Shipments of 226.8 kg (500 lb) drums of solid sodium dichromate dihydrate were received and stored at the 185-D Building from 1955 until 1959. Based on historical information for the 1713-DA Essential Materials Warehouse, supplies of 45 kg (100 lb) bags of solid sodium dichromate dihydrate also may have been stored at the 1713-DA Essential Materials Warehouse from 1944 until about 1955. It is not known when the 1713-DA Building was removed, but it was not seen in aerial photos after 1955. The shipments of bags and drums of solid sodium dichromate dihydrate were replaced with shipments of 70 wt% sodium dichromate water solutions beginning in 1959 and continued until the 105-D Reactor was shut down in 1967. In 1959, a tank truck/railroad car Unloading/Transfer Station (100-D-12) was installed adjacent to the railroad spur between the 183-D and the 183-DR Water Treatment Plants. The concentrated sodium dichromate solutions were transferred by hose from railroad cars or tanker trucks to the pumping facility (100-D Area Technical Baseline Report [WHC-SD-EN-TI-181]).

The bag-mixing process in the 190-H Building used solid sodium dichromate from 1949 to 1959 and 70 wt% sodium dichromate solutions from 1959 to 1965. In 1959, a 56,781 L (15,000 gal) horizontal storage tank was installed in the 190-H Building to receive, store, and supply a 70 wt% sodium dichromate solution to the batch mixing tanks also located in the 190-H Building.

The delivery of the 70 percent solution into the storage tanks was not completely efficient, and yellowish-stained soil around the storage tank location indicated losses to the subsurface. In addition, some leakage in the transfer pipes or connection between the transfer pipes and the mixing tanks is plausible. The fraction of delivered 70 percent solution lost to the subsurface is not known at either 100-D or 100-H.

- Following discharge of these concentrated Cr(VI) fluids into the subsurface, vertical migration occurred. The density of the fluid would have facilitated vertical migration into the subsurface with little lateral movement. However, very little information is available that describes the initial distribution of Cr(VI) from this fluid in the subsurface; and several factors suggest a broad range of possibilities. The vadose zone and the unconfined aquifer are about 25 m (82 ft) and generally 8 to 12 m (26 to 39 ft) thick, respectively, near 100-D-100. Column studies conducted by PNNL show an initial large fraction of Cr(VI) leaching in the first pore volume followed by diminishing returns, as the additional leachate contains increasingly smaller fractions tending asymptotically to zero.
- The current RTD remediation strategy in the vadose zone appears to be protective once contaminated soils are removed from the affected waste sites. However, the potential remains for residual contamination within unremediated portions of the vadose zone, particularly near historical release points that produced groundwater contamination. Undefined secondary sources could gradually leach into the groundwater for a number of years and will be monitored in the groundwater. There remains uncertainty in how this residual contamination might behave within 100-D/H.

The practice of disposing high volumes of liquid waste to waste facilities not only created a groundwater mound but also, because the water was contaminated with Cr(VI) and fission products, caused widespread distribution of contaminants underlying 100-D/H.

Residual contaminants with higher K<sub>d</sub> values (less mobile) may be retained within the vadose zone at, or near, historical release points. These contaminants may be mobilized and reach the water table under the driving forces of seasonal precipitation recharge or transient anthropogenic recharge events. The 100-D/H Work Plan identified several locations where the source areas in the shallow vadose zone had been remediated but where the potential remained for residual contamination below the depth of remediation. Several characterization boreholes and wells were drilled at these locations to evaluate the presence of

residual contamination; these results indicated no mobile constituents (beyond those already identified) are found beyond the depth of excavation or below the water table and no deep contamination was found that constitutes a groundwater or surface water protection issue. Groundwater contaminants that do not warrant further evaluation in the FS, but have infrequent detections above an action level will be included in the RD/RAWP for the purpose of continued monitoring at appropriate locations and frequency. Following are potential locations for this type of source:

- Cr(VI)-contaminated vadose zone soil underlying the sodium dichromate solution transfer facilities associated with the water treatment chemical handling at 105-D, 105-DR, and 105-H Reactors. Specifically, these areas of interest are near the 108-D Building and its associated liquid waste cribs, the overhead and underground pipelines that transferred concentrated sodium dichromate solutions between 108-D Building and the 183-D and 183-DR Head Houses, and the former railcar unloading station identified as 100-D-12. These areas are likely to have contributed to other constituents present in soil and groundwater that are not identified as COPCs (for example, sodium, aluminum, and sulfate). Remediation activities near these facilities have identified contamination present throughout the entire thickness of the vadose zone.
- Vadose zone soil underlying the various liquid process waste disposal facilities at the 105-D, 105-DR, and 105-H Reactors (that is, cribs and trenches).
- Vadose zone soil beneath the reactor cooling water retention basins and discharge facilities at 100-D/H. The soil may contain residual Cr(VI), fission products, and other cooling water-related constituents.
- Vadose zone soil underlying the fuel storage basins and the basin leak disposal cribs/injection wells, contaminated with Cr(VI) and mixed fission products (for example, strontium-90, tritium, Cs-137) (presented in Section 1.2.2). This is supported by the continued presence of the strontium-90 plume near the fuel storage basin.

Based on observations and measurements of site-related contaminants, contaminated groundwater beneath the 100-D/H Reactor areas may be a pathway of contamination discharging to the river and to the riparian/river shore area during high river stage. Prevention of the pathway from groundwater to surface water is a key consideration in the FS.

### 4.9.8.2 Periodically Rewetted Zone

The PRZ is the portion of the vadose zone and aquifer system that lies between the seasonal high and low groundwater elevation levels. This zone has the potential to function as a secondary source for some contaminants, particularly those that exhibit  $K_d$  values greater than 1 ml/g. Contaminants may enter the PRZ under two common conditions: by downward migration from an overlying vadose zone source, or by emplacement from contaminated groundwater during high water conditions, where the contaminant(s) may be retained by the soil matrix in that zone, and then re-enter the groundwater at the next high water period. The rate of contaminant migration from the overlying vadose zone is highly influenced by the presence of silt and clay layers, which may impede the vertical transport of contaminants resulting in a slower response in groundwater, primarily for less mobile contaminants. Layering may result in a longer pathway from the surface to groundwater, resulting in an extended time frame for impacts to occur. Migration of highly mobile contaminants is unlikely to be notably affected by these zones, regarding time frame, but the contaminant footprint in the soil column may be increased by such migration laterally. Contaminants within the PRZ may be retained by various mechanisms, including ion exchange processes, or simply by retention of contaminated water within small pore structures by capillary action when water levels decline.

As groundwater rises into the PRZ during high water, groundwater may contact contaminants that are present in the overlying soil. As the water table falls, the contaminant may leach out of the soil and migrate into the aquifer below. This rewetting action thereby allows for potential ongoing release of contaminants to the groundwater. The rate of downward migration through the vadose zone depends on the K<sub>d</sub> value of that COPC and the presence of driving forces, such as water.

Examination of the time series of Cr(VI) concentrations, a highly mobile contaminant, and the associated groundwater elevation hydrograph for a well near the highest-concentrated portion of the plume underlying 100-D (i.e., Well 199-D5-99) shows the effect of this rewetted zone. In Well 199-D5-99, the Cr(VI) concentration reaches its maximum transient concentration in the period following seasonal maximum transient groundwater elevation (Figure 4-121). Groundwater rising into the overlying zone of soil contamination increases the rate at which contaminants are leached to the groundwater, causing a temporary peak in concentrations. Contaminants with higher  $K_d$  values would also tend to leach, but at significantly lower rates, as discussed in Section 5.

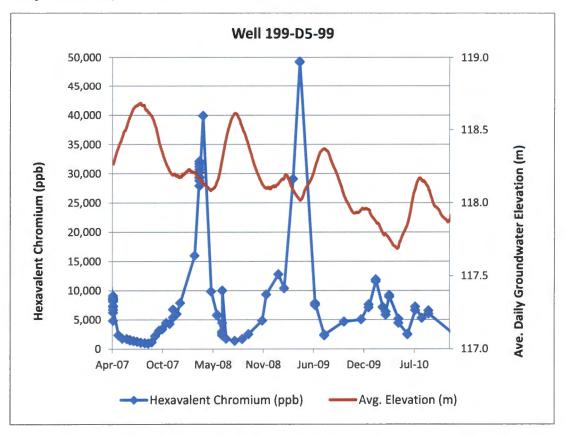


Figure 4-121. Cr(VI) Response to Groundwater Level Changes in Well 199-D5-99

The delayed response shown by Cr(VI) at Well 199-D5-99 is a result of both the distance of the well from the river, and the fact that the water table is present within the less permeable or transmissive Ringold Formation unit E, which slows the response. In addition, at average water table elevations, the lower zone would be flushed of contaminants on a regular basis meaning that only higher water periods would introduce the overlying contaminant into the groundwater. At 100-H, this response is also present (as in Well 199-H4-4), even though there appears to be less of a delay since the well is close to the river and the aquifer is within Hanford formation material.

Ongoing remedial actions at the 100-D-100 unplanned release site suggest that Cr(VI) is present in the vadose zone throughout the soil column thickness. In addition, because the Cr(VI) at the groundwater interface is localized, the fluctuations in Cr(VI) concentrations in groundwater from Well 199-D5-99 are likely more directly related to the vadose source and not specifically a source in the PRZ. An increase in Cr(VI) concentrations in groundwater may be experienced in areas where the source material remains and surface water is applied, source area excavation timeframes are extended, or deep excavations are open for extended timeframes. A potential response to surface water application is seen in the increase of Cr(VI) concentrations in Well 199-D5-103, located downgradient of waste site remediation. However, near waste site 100-D-100, which is also undergoing remediation: well 199-D5-104 showed minor fluctuations in concentrations that are likely seasonal; well 199-D5-39 has a downward trend; and nearby well 199-D5-97 also had a decreasing trend in Cr(VI) concentrations. Mobile contaminants located within the PRZ are most likely a continuation of the residual, overlying contamination in the vadose zone.

Strontium-90, which has a higher K<sub>d</sub>, exhibits some seasonal variations at 100-H, apparently related to changes in water table elevation. The response to groundwater fluctuations and associated change in the shape of the plume indicates the presence of strontium-90 in the soil above the aquifer. In addition, discontinuous low-level detections of strontium-90 have been measured in groundwater in the immediate vicinity of 105-DR Reactor. As not all waste sites have been remediated near the likely sources, it is not yet clear if strontium-90 is present throughout the vadose zone or in the limited area near the water table.

#### 4.9.8.3 Groundwater

In the unconfined aquifer, groundwater impacts at 100-D/H are primarily due to contaminated cooling water. However, elevated Cr(VI) concentrations at 100-D also indicate that some fraction of the 70 percent solution has reached the unconfined aquifer. The maximum Cr(VI) concentrations in a number of wells exceed reactor coolant chromium concentrations (up to  $700 \, \mu g/L$ ) at the 100-D southern hot spot. These wells have shown Cr(VI) levels up to  $69,700 \, \mu g/L$ , concentrations that could not be achieved if the source were the reactor coolant only.

The lower concentration, but very high volumes of cooling water that were discharged during operations resulted in spreading Cr(VI) and other analytes over a broad area since the cooling water mound flowed with groundwater. Groundwater flow during operations was generally toward the east (Figure 3-54), with some component of flow at 100-D being more westerly, toward the Columbia River. During the 1967 infiltration test, this flow direction was accentuated, with the high hydraulic head of the mound forcing water through the aquifer at a higher than normal rate, and hydraulic head.

Groundwater monitoring data indicate that Cr(VI) from concentrated solution is present at the 100-D south plume. The flow path of the high concentration plume is consistent with groundwater flow direction. In addition, while the concentrations of Cr(VI) have been as high as 69,700 µg/L at the south plume, the density does not appear to control the movement of the contamination. Depth discrete data collected during the RI and during previous investigations indicate that, while there is uneven distribution of Cr(VI) in the unconfined aquifer, it is not consistent throughout the aquifer. Current pump-and-treat operations are greatly reducing the Cr(VI) concentrations in this area, as exhibited in Well 199-D5-122. These same pump-and-treat systems also serve to control groundwater flow by creating artificial, relatively small groundwater mounds and sinks. A small groundwater mound is also still present at the 182-D Reservoir due to leakage.

Contaminants near the bottom of the unconfined aquifer do appear to have been influenced by the depressions identified in the RUM surface. The undulating surface of the RUM (Section 3.4.2) has a marked depression that coincides with the 100-D southern Cr(VI) plume hot spot (Figure 3-4). The depression extends to the south and then curves to the west and toward the Columbia River. Analytical

results from Well 199-D3-5 (C7620, Well 2), where the highest Cr(VI) in the well is at the top of the RUM surface, can be explained by contaminants following the RUM surface (Section 4.5.1 – Vertical Distribution of Cr(VI)). Contaminants within a low spot would also experience lower flow rates and would not disperse as readily as in the upper portions of the aquifer.

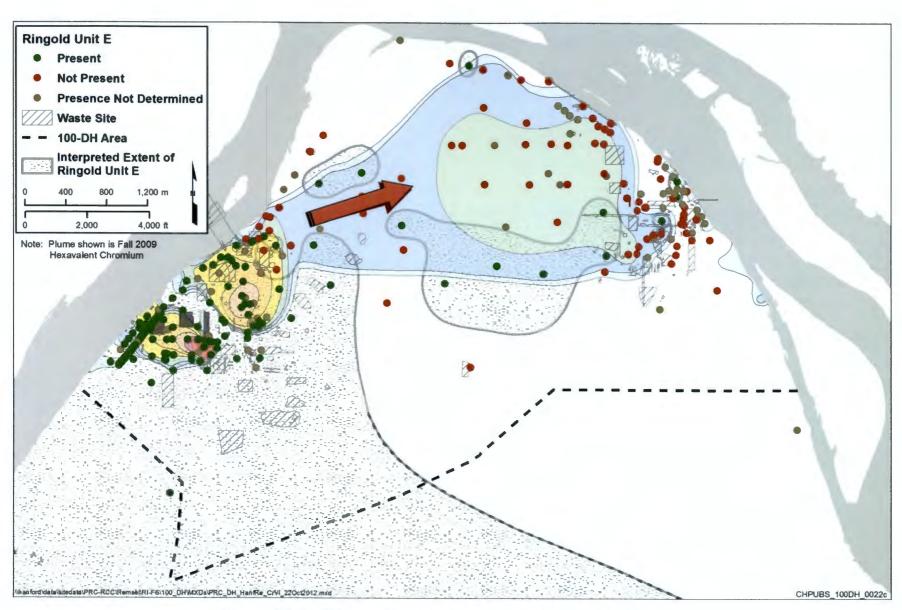
Groundwater flow across the Horn is primarily controlled by the hydrogeology of the area. The Ringold Formation unit E is the primary material of the unconfined aquifer at 100-D. Within the Horn, the unconfined aquifer occurs primarily within the Hanford formation, as it is at 100-H. However, in some areas of the Horn, erosional remnants of Ringold Formation unit E are present. Since groundwater flows more easily through the Hanford formation due to hydrogeologic properties, a preferred pathway would have been created for contamination movement from 100-D across the Horn. As shown conceptually on Figure 4-122, the presence of Ringold Formation unit E may have directed flow (as shown by the arrow) across the Horn to 100-H.

Cr(VI) contamination is also present in areas where there is Ringold Formation unit E present. This is theorized to be a result groundwater rising above the Ringold Formation unit E during extremely high groundwater periods. As the amount of cooling water discharge increased, such as during the 1967 test, contaminated cooling water potentially overtopped the Ringold/ Hanford contact elevation due to the exaggerated groundwater mound.

The groundwater mound also had the effect of displacing the original groundwater volume in the unconfined aquifer with cooling water effluent. Contaminants related to cooling water, such as Cr(VI) and fission products, were distributed throughout the unconfined aquifer and up into the deeper vadose zone. As the mound collapsed, contaminants with higher  $K_d$  values would have been stranded in the lower portion of the vadose zone. Contaminants with high  $K_d$  values can be retained by various sorption processes onto the silt, sand, and gravel matrices within the aquifer (saturated conditions). These contaminants may continue to enter groundwater by dissolution, diffusion, or ionic exchange processes but likely at a very low rate. In areas where groundwater moves very slowly (for example, most of the 100-D area), high concentrations of contaminants adsorbed on the aquifer matrix may slowly diffuse and disperse into groundwater as it interacts with the affected matrix, resulting in persistent downgradient distribution of elevated contaminant concentrations in groundwater. This is most likely to have occurred in the area between the 116-DR-1&2 Trench and the middle of the Horn, where the drop in water levels during collapse of the mound would have been greatest.

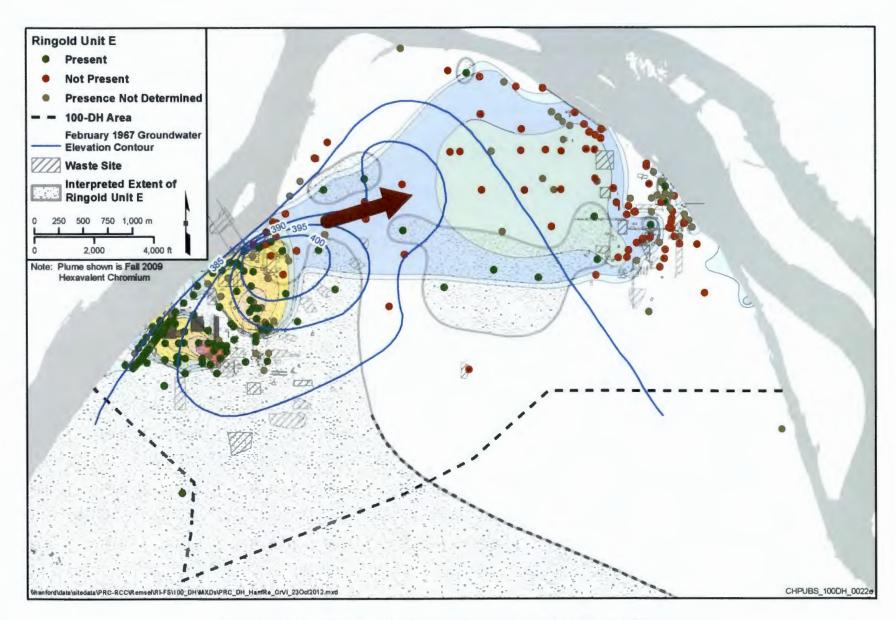
The first water bearing unit within the RUM has been identified as contaminated in several locations. The RUM consists of gravel in a silt/clay matrix and is considered an aquitard, a leaky confining unit with limited groundwater movement. Within the RUM, thin sand/gravel lenses form discontinuous water-bearing units with variable transmissive properties. Along with variations in RUM surface topography, there is also variation in the thickness of the silt/clay units between the various water-bearing units of the RUM.

Samples collected from water-bearing units within the underlying RUM unit did not exhibit site-related contamination at 100-D. Farther to the east, within the Horn, contamination has been identified in the RUM at Well 699-97-48C. This well is located downgradient from the discharge point for 105-D and 105-DR cooling water during the 1967 infiltration test and would have experienced high hydraulic head conditions, forcing contaminated cooling water into this unit. As shown in Figure 4-123, this theory is supported by the water table elevation from operations, which shows a preference for water movement near Well 699-97-48C. The well is located between two remnants of Ringold Formation unit E, which would have acted as a "pinch point" for groundwater moving eastward through that area.



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Figure 4-122. Cr(VI) Plume with Geologic Formations of the Unconfined Aquifer



4-302

Figure 4-123. Cr(VI) Plume with Geologic Formations of the Unconfined Aquifer

Aquifer tests (see Chapter 3, Section 3.7.4) and geochemistry analysis (Section 3.7.6) indicate that a hydraulic connection exists between the first water-bearing unit in the RUM and the Columbia River near Well 199-H4-12C, and Well 199-H4-15CS. Based on boreholes placed near the 105-H Reactor, the upper confining portion of the RUM appears to thin at this location, likely caused by shallow sediments being reworked and eroded by flood events. These wells coincide with a downward slope of the RUM surface toward the river, located just east of the 183-H Solar Evaporation Basins.

During the RI, several wells were drilled into the first water-bearing unit of the RUM. Contamination was identified in this unit at 100-H, with Cr(VI) concentrations as high as 287 µg/L in a groundwater sample collected during drilling of Well 199-H3-9. However, a comparison of the RUM thickness to the Cr(VI) concentrations did not show any obvious pattern. An analytical model of the RUM contamination was developed (Evaluation of Potential Hydraulic Capture and Plume Recovery from the Ringold Upper Mud (RUM) in the 100-HR-3 Operable Unit (OU) [ECF-100HR3-12-0025] in Appendix F) to assess the current state of capture from the two pumping wells in this unit (discussed in the FS).

Groundwater generally moves through the Hanford formation with the direction of flow determined by seasonal variations in the water table inland from the river and in response to Columbia River stage variations. During the high-river stage period in early to mid-summer, groundwater flows southeasterly across the northern portion of the Horn area; during periods of general low river stage, groundwater generally discharges into the Columbia River from inland areas. Erosion of the Ringold Formation unit E and parts of the RUM in the Horn area have created an undulated RUM surface topography that may expose some of the water-bearing units within the RUM, particularly in the northern portion of the Horn area. This condition may account for the historical entry of contaminants (for example, Cr(VI)) into shallow water-bearing units of the RUM, as observed at some localized portions beneath the Horn area.

The groundwater flow system beneath the Hanford Site remains a primary pathway for contaminants to migrate away from source areas and, for some contaminants, to discharge into the river. Characterization of hydrogeology at the 100 Area requires understanding of the properties and behavior of the vadose zone, groundwater, and surface water sources, interfaces, and interactions. Both natural and anthropogenic hydrologic processes have influenced groundwater flow patterns and contaminant distribution in the subsurface underlying 100-D/H. The effects of natural processes on contaminant migration are ongoing, while the effects of anthropogenic operations (for example, the high-volume liquid discharges into the 116-H-7 Retention Basin, 116-H-1 Trench, 116-D-7 and 116-DR-9 Retention Basins, and 116-DR-1 and -2 Trenches) have diminished over time with the cessation of reactor operations.

However, some residual effects have not completely dissipated, and other processes continue to influence contaminant migration, particularly ongoing pump-and-treat operations.

Groundwater flow directions close to the Columbia River are influenced by river stage. Generally, natural groundwater flow patterns transport COPCs toward the Columbia River. Groundwater flow toward the river dominates at low river stage and surface water dominates the near-shore aquifer flow during periods of peak high river stage. In spring, when the river stage is high, the water table near the river flattens and river water may flow a limited distance into the unconfined aquifer. High river stages can be more than 4 to 5 m (13 to 16 ft) greater than low river stage. The river stage can also fluctuate several meters over short periods (that is, hours to days), based on Priest Rapids Dam operations. River stage fluctuations influence groundwater elevations and flow directions several hundred meters inland from the river. The magnitude of the influence is tempered with increasing distance from the river. Groundwater flow through the first water-bearing unit in the RUM is tempered by recharge water having to move more slowly through sediments with lower hydraulic conductivities of 1 × 10<sup>-7</sup> cm/s. As a result, the groundwater flow within the RUM is much slower and Cr(VI) will have a longer residence time.

*Important Groundwater Concepts.* Groundwater flow and contaminant fate and transport processes beneath 100-D/H are highly complex. The main concepts regarding contaminant effects in groundwater include the following:

- Remaining contamination at 100-D/H is primarily associated with Cr(VI) in the following general locations:
  - The high concentration 100-D south plume, which is apparently associated with stock solution releases at 100-D-100, no high concentration source area has been identified at the 100-D north plume.
  - The Cr(VI) plume within the unconfined aquifer underlying 100-D and the Horn originated from 105-D and 105-DR Reactor operations. Most of the effect to the Horn likely occurred during the 1967 infiltration test at 116-DR-1&2, associated with the 105-D Reactor.
  - Relatively low concentrations across the Horn associated with the 116-DR-1&2 Trench 1967 infiltration test.
  - The first water-bearing unit in the RUM in the Horn (slightly east of 100-D) at Well 699-97-48C was likely affected from the 116-DR-1&2 Trench and 1967 infiltration test. The effect appears to be limited in areal extent to a small area of the Horn, and also limited to low concentrations of Cr(VI).

Contamination in the first water bearing unit of the RUM at 100-H, which is likely associated with the 100-H groundwater mound during operations.

- The Cr(VI) plume within the unconfined aquifer underlying the western portion of 100-H originated from 105-D and 105-DR Reactor operations. Cr(VI) contamination in the unconfined aquifer along the eastern portion of 100-H was a result of 105-H Reactor operations and has been largely remediated.
- Natural attenuation of Cr(VI) is largely attributed to the reduction to Cr(III), with some adsorption and precipitation. The formation of low-solubility Cr(VI) salts may also occur in the environment. Adsorption may facilitate the reduction process. Reductants associated with the aquifer matrix are most important; iron is an important component that is abundant within Hanford sediments. Much smaller plumes of nitrate and strontium-90 are also present in 100-D/H.
- The first water-bearing unit of the RUM at 100-H was affected from 105-H Reactor operations and the resultant groundwater mound. This may be associated with the thinner aquifer and the absence of the Ringold Formation unit E at 100-H, compared to 100-D.
- The interim action DX/HX pump-and-treat system continues to decrease the areal extent of Cr(VI) and reduce Cr(VI) concentrations in the unconfined aquifer.
- Contaminants that are collocated with Cr(VI), such as nitrate, are also being removed from the aquifer by the pump-and-treat system. This aspect is important for remedy selection and design.

# 4.9.8.4 Hyporheic Zone

The hyporheic zone is a significant interface where groundwater transitions from the aquifer into the surface water. The CRC (DOE/RL-2010-117) evaluated contamination within this zone, and associated ecologic risks are discussed in Section 7.6.4.5. It can be characterized in physiochemical terms by the presence of at least 10 percent advected stream water in the subsurface ("Retention and Transport of

Nutrients in a Third-Order Stream in Northwest California: Hyporheic Processes" [Triska et al., 1989]) and can be considered a temporally dynamic area of subsurface mixing between the surface water and groundwater beneath and laterally to a stream channel.

The hyporheic zone in the immediate vicinity of the river is monitored at 100-D/H by analysis of samples collected from a series of shallow sampling structures colloquially called aquifer tubes. The aquifer tube samples have confirmed the presence of 100-D/H contaminants in subsurface water in this zone. Concentrations are variable and somewhat dependent on river stage at the time of sampling. When the river stage is high and river water is actively entering a bank storage condition, concentrations tend to be at their minimum. When river stage declines, contaminant concentrations typically increase as the river once again becomes a gaining stream receiving discharge of groundwater from beneath 100-D/H.

The water particle flow direction moves according to river stage. At high river stage, flow paths are away from the river. When flow reverses, flow should approximately follow the same streamline in the opposite direction with potentially a small component of deflection downstream. "Influence of Oscillating Flow on Hyporheic Zone Development" (Maier and Howard, 2011) indicates that a daily stream stage fluctuation of 0.8 m (2.6 ft) generates between 1.75 and 2.5 m (5.7 and 8.2 ft) of particle movement into and out of the stream bank, and 1.25 to 1.5 m (4 to 5 ft) within the riffle. For streams with a daily stream stage change of 4 m (13 ft), which can occur on the Columbia River, the particle oscillation into the bank extends as much as 7 m (23 ft) while the vertical particle movement within the riffle is only between 3 and 3.5 m (10 and 11.5 ft). During this process, surface water infuses into the hyporheic zone and shoreline portion of the aquifer. River water refreshes some mineral surfaces and provides additional nourishment to bacteria in the form of organic carbon, phosphates, and other nutrients.

Under steady-state flow conditions, flow paths are generally smooth and residence times of surface water in the hyporheic zone are relatively long. Stream-stage fluctuations create fluctuating head gradients and flow reversals, depending on the magnitude of the stream-stage fluctuation ("Influence of Oscillating Flow on Hyporheic Zone Development" [Maier and Howard, 2011]). As demonstrated by aquifer tube and near shore monitoring well data collected during higher river stages (which indicates very low or non-detectable concentrations), the Cr(VI) in the near shore environment is pushed inland away from the river. The oscillating particle effect demonstrated by "Influence of Oscillating Flow on Hyporheic Zone Development" (Maier and Howard, 2011) for rivers with more extreme fluctuations of stream stage results in a more dynamic exchange of biological and chemical parameters, including iron.

### 4.9.8.5 River/Riparian Zone

The riparian zone along the river is subject to periodic flooding and deposition of sediment and other detritus along with the floodwater that contains contaminants from upstream. This includes both the immediately upstream portions of the Hanford Site as well as the main upstream flow from Canada and northern and central Washington. Therefore, non-Hanford Site contaminants may be introduced to the surface, vadose zone, and groundwater portion of the riparian zone through flooding. Most recently, significant riparian flooding was observed in 2011 as a result of the high run-off associated with the 2010 to 2011 snow pack.

Over the years of the Hanford Site operations, direct discharges also have affected the river. Data from the Columbia River RI Work Plan (DOE/RL-2008-11) and *DQO Summary Report for the Remedial Investigation of Hanford Site Releases to the Columbia River* (WCH-265) suggest historical discharge from 100-D/H operations affected the Columbia River. Large quantities of cooling water were discharged directly to the river via outfall pipes. Upstream data indicate that industrial and mining sources also contributed contaminants to the Columbia River.

Upwelling studies showed several locations where measurable Cr(VI) was upwelling in the riverbed adjacent to the known groundwater plumes in 100-D/H. Evaluation of the flow regime on both sides of the river indicates that groundwater from 100-D/H does not upwell beyond the thalweg on the far side of the river. The upwelling studies (Columbia River RI Report [WCH-380]) indicate that during low flow stage in the river, water that is largely Hanford Site groundwater can upwell into the river. Given the large diurnal changes in river stage, this upwelling condition is likely to be ephemeral as groundwater flow reverses direction into and out of the river several times per day in response to operations upstream at Priest River Dam.

### 4.9.8.6 Pathways

A final aspect of the CSM is the different exposure pathways in which humans, animals, and plants could potentially be affected by the presence of contaminants in the environment. The exposure pathways and risk assessments for humans are described in Chapter 6 and the exposure pathways and risk assessments for biota are described in Chapter 7. The remedies are developed and evaluated in Chapters 8, 9, and 10; the remedies are chosen to break the exposure pathways, thereby providing effective mitigation of the potential risks that the contaminants pose. The general CSM elements that describe the full evolution of contaminants in the environment are described in Chapter 1 and are represented in the flow diagram on Figure 4-124.



Figure 4-124. Simplified CSM Element Diagram

The potential exposure points for contaminants in soil and water are determined by the location of the contaminants and the potentially applicable transport mechanisms. The following potential exposure points are identified for contaminants at 100-D/H:

- The ground surface within 100-D/H at areas where contaminated soil is located in the surface, or near-surface, such that exposure could occur by transient contact with surface soil, or through minimally intrusive activities.
- The subsurface portion of the vadose zone within 100-D/H where contaminated soil may be
  encountered during intrusive activities (for example, excavation for construction). Excavation
  activities can also relocate contaminants to the ground surface where they may become subject to
  surface exposure.
- Food chain effects may occur where contaminants from the surface or subsurface soil are taken up by
  plants or animals, thereby entering the food chain. This incorporates two types of potential exposures:
  direct contact and ingestion by the initially exposed organism(s), and subsequent exposure to second
  order consumers by ingestion of the contaminated organisms.
- Contaminated groundwater beneath 100-D/H could potentially be extracted and consumed, thereby creating an exposure point for contaminated groundwater potentially anywhere within the aquifer where it would be feasible to produce a useful volume of water.
- Contaminated groundwater at locations outside 100-D/H where contaminants may migrate from the source area. This groundwater could potentially be extracted and consumed, thereby creating an

exposure point for contaminated groundwater potentially anywhere within the aquifer where it would be feasible to produce a useful volume of water.

- Surface and subsurface soil within the riparian zone near the river where contaminants may migrate via overland flow of contaminated groundwater discharging seasonally from seeps above the river stage elevation.
- Surface water of the Columbia River adjacent to, and downstream from, 100-D/H, where contaminants migrate from the site via overland flow processes or by the interaction of contaminated groundwater with surface water of the river.

The CSM summarizes the primary and secondary sources of contaminants at 100-D/H, the mechanisms for contaminant release into the environment, and contaminant distribution through the environment. The migration of contaminants includes a discussion on the driving forces and transport mechanisms whereby contaminants have a pathway to cause exposure to a receptor. The evaluation of risk from contaminants is provided in Chapters 6 and 7. This evaluation provides a basis for a remedial action to break the pathway for exposure for a contaminant that poses a risk to human health or the environment. The evaluation of potential remedies is presented in Chapters 8 through 10.

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# 5 Contaminant Fate and Transport

This chapter presents an evaluation of the anticipated behavior of selected contaminants in the vadose zone and groundwater at 100-D/H. An approach is presented for the assessment of anticipated future behavior of vadose zone contaminants that may function as secondary sources of contamination. The approach describes how these contaminants are released into the environment to affect underlying groundwater. A simulation approach is also presented to describe the future behavior of contaminants already present in groundwater at 100-D/H. Factors affecting the fate and transport of contaminants and results, and uncertainties in the information and methods are discussed, concluding with a summary of the chapter as a whole.

The purposes of the fate and transport information provided in this chapter are as follows:

- Describe the development of SSLs and PRGs for contaminated vadose zone soil remaining after remedial action in 100-D/H. In addition, the chapter will describe the application of the SSLs and PRGs to observed soil conditions to support assessment of potential threats to groundwater and surface water.
- Use the SSLs and PRGs to evaluate whether contaminants present in the vadose zone at 16 waste sites characterized during this RI and during the
  - preceding LFI, as well as interim closed waste sites, may act as a secondary source of groundwater contamination. Waste sites that are not yet remediated were carried forward into the FS for evaluation without SSL/PRG evaluation with the COPCs identified for those waste sites based on process knowledge.
- Establish a process for evaluating ongoing groundwater and vadose zone remediation activities and comparing remedial alternatives being considered for completing cleanup actions at 100-D/H.

Understanding contaminant fate and transport in the environment is an important part of the RI/FS process. Projections of future contaminant behavior and concentrations at points of exposure are needed to assess potential threats to human health and the environment. These simulations are especially important for sites where contaminants are long-lived or where groundwater contaminant plumes may migrate beyond the area covered by a monitoring well network. Contaminant fate and transport was simulated using a one-dimensional (1D) computer model for the vadose zone and a three-dimensional (3D) computer model for groundwater contaminants. These simulations are used to describe how contaminants may behave in the vadose zone for post-remedial conditions, and in the groundwater for baseline conditions; the same groundwater model is used in the FS to evaluate remedial alternatives. Additional modeling may be used to simulate contaminant fate and transport in the future, which will be described as part of the RD/RAWP.

This chapter describes key processes affecting the fate and transport of 100-D/H COPCs in environmental media, and the effect these processes have on the distribution of COPCs in the future. The information

### Highlights

- The disposal of large volumes of liquid effluent to the vadose zone during reactor operations resulted in accelerated transport of contaminants to deeper portions of the vadose zone and the unconfined aquifer in 100-D/H.
- Contaminant migration rates are currently much slower, because liquid effluent discharges have stopped.
- For previously remediated waste sites, there were no exceedances of soil screening levels protective of groundwater and surface water.
- Groundwater contaminant flow and transport modeling indicates that the groundwater pump-and-treat systems provide protection to the Columbia River along the shoreline in almost all areas.
- The existing groundwater pump-and-treat systems are actively remediating the Cr(VI) plumes.
- Strontium-90 and nitrate concentrations in 100-D/H groundwater above the MCLs are within the capture zone of the recovery wells. Concentrations and plume footprint areas in groundwater will decline over time, although the rate of decline is not uniform across the area.

presented in this chapter was used to calculate SSLs and PRGs that are protective of groundwater and surface water under the modeling scenarios presented. Remediated waste site constituent concentrations are compared to the SSLs and PRGs to identify waste sites requiring consideration in the FS for groundwater or surface water protection. The results from groundwater flow and transport models developed to simulate existing COPC fate and transport in groundwater for the 2011 through 2087 period are also presented. Simulation duration is based on the time required for the maximum contaminant level to decline below the cleanup level for all COCs, with the exception of Cr(VI). The predicted maximum contamination level for Cr(VI) is still well above the cleanup level after 77 years and the rate of decline strongly indicates it will not decline to cleanup levels in 100 years under the no-further-action case. Accordingly, it was deemed unnecessary to extend this simulation further in time in order demonstrate the no-further-action scenario was inadequate as a remedial option for Cr(VI). The assumptions and model input parameters detailed in this chapter are important for future waste site remediation efforts and meeting the cleanup standards. The cleanup verification process, including demonstration of how cleanup standards are achieved, can involve the evaluation of the conceptual site model at the individual waste sites against the assumptions used to develop the SSLs and PRGs. To the extent a significant deviation from the groundwater/surface water protection SSLs and PRGs assumptions is observed, site-specific conditions can be used to revise the fate and transport models to evaluate the potential for the waste site to act as a source of groundwater contamination.

A total of 127 interim remediated and three unremediated waste sites were evaluated to determine if further action might be needed for the protection of groundwater and surface water. No waste sites exhibited exposure point concentrations (EPC) greater than the SSLs. None of the EPCs for metals fell outside the reported background concentration range for Hanford Site soil types.

Uranium is not modeled for purposes of evaluating SSLs and PRGs because it is not a soil COPC at 183-H or other 100-D/H locations, therefore modeling is not required (Section 4.4.1.2).

The remaining waste sites that are not yet remediated are carried into the FS for evaluation. The COPCs identified for those waste sites are based on process knowledge.

# 5.1 Evaluation Process for Assessment of Protectiveness of Groundwater and Surface Water

The evaluation of the potential for vadose zone contamination to affect groundwater and/or surface water followed a specific set of logical steps shown on Figure 5-1. This process evaluated the potential for secondary source contaminants to migrate to groundwater and subsequently discharge to surface water at concentrations that would pose a threat to human or ecological receptors. This evaluation did not include assessment of potential for effects of direct contact exposures to shallow or surface contamination (direct contact exposure assessment is provided in Chapter 6). The activities associated with these steps are as follows:

• Available data that describe the nature and extent of residual vadose zone soil contamination at a particular waste site were assembled. This included laboratory analysis of soil samples collected from the vadose, field measurements of specific contaminant concentrations, qualitative and quantitative measurements of radionuclides present in the vadose zone, measurements of soil physical properties (for example, moisture, particle size distribution), and field observations during drilling and/or excavation. These data were generated from process knowledge and operating history, from specific waste site characterization activities (for example, LFIs and RI activities), or from completion and verification measurements (CVP) associated with completion of vadose zone remedial activities.

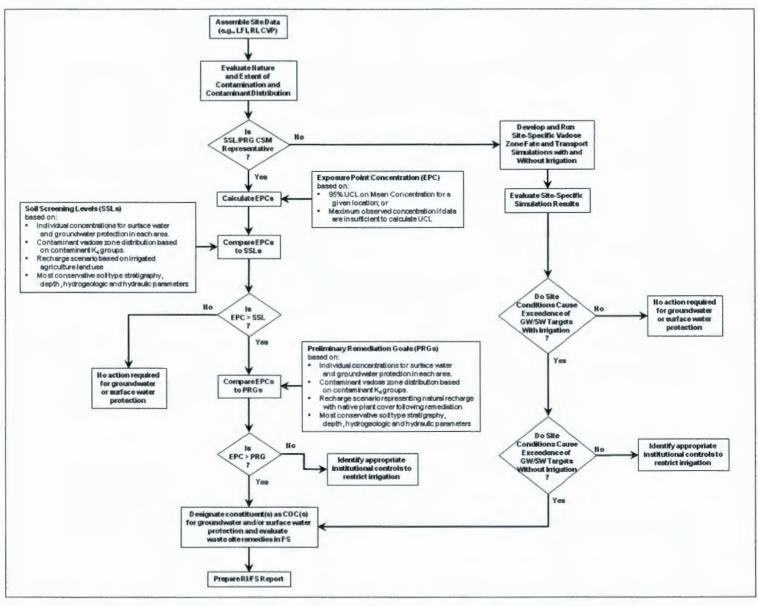


Figure 5-1. Process for Evaluation of Post-Remediation Site Measurement Data for all COPCs for Groundwater and Surface Water Protection

- The data were assembled to provide a description of residual contamination conditions that included concentrations of contaminants and their locations with the vertical and horizontal extent of the waste site.
- The individual waste site conditions were then compared to the generic conceptual site models developed for the SSL and PRG development. If the known site conditions were similar to those used to describe the SSL and PRG simulations (that is, 100:0 or 70:30 profile, depending on individual contaminant's K<sub>d</sub> value), then the evaluation followed the SSL and PRG comparison pathway. If, however, the known site conditions differed from the default simulation such that these were non-conservative initial conditions, then the waste site was evaluated using a site-specific contaminant transport simulation. Conditions indicating that default scenarios are not representative included the presence of past or persistent groundwater plumes associated with a specific waste site or operating area or an observed vertical distribution of a contaminant, or contaminants, within the vadose zone that were inconsistent with the default initial distribution (that is, 100:0 or 70:30 profile), such that the default initial condition would be nonconservative with respect to peak groundwater concentration for that contaminant.
- Waste sites for which the default conditions were not representative were subsequently evaluated individually in a site-specific analysis.
- EPCs were derived for each COPC based on the site-specific data at hand, and were assigned either
  the 95 percent UCL on the mean concentration or the maximum observed concentration if available
  data were insufficient to derive the 95 percent UCL.
- The EPCs for each contaminant at a waste site were then compared to the SSLs. The SSLs represent protection values (protective of groundwater and surface water) for screening use based on the maximum reasonably foreseeable recharge scenario in the I00 Area (that is, irrigated agriculture). If the EPC is less than the SSL, then that contaminant was identified as requiring no further action and the assessment moved on to the next contaminant.
- If the site-specific contaminant EPC exceeded the SSL, then the EPC was subsequently compared to the PRG for that contaminant. The PRGs represent protection values (protective of groundwater and surface water) based on the expected land use in the 100 Area (that is, conservation activities with native vegetation). If the EPC exceeded the SSL, but was less than the PRG, then the affected waste site was identified for application of institutional controls that will prevent irrigation in the future at the site. If the EPC exceeded the PRG, then the contaminant was identified as a COC and the site was included in the FS for identification of appropriate remedial alternatives to mitigate risks to groundwater and surface water posed by the vadose zone contamination.

In cases where the waste site conditions were not adequately represented by the default SSL and/or PRG simulations, then the waste site and its affected contaminants were evaluated using a site-specific vadose zone transport simulation. This simulation used the same general fate and transport modeling approach used for the SSL and PRG development, except that site-specific conditions were substituted where appropriate. Site-specific simulations were evaluated as follows:

Site-specific results under the irrigation recharge scenario were evaluated to determine if the site
conditions resulted in exceedance of the contaminant-specific groundwater or surface water
protection criteria (for example, MCLs or AWQC). If the site conditions did not cause an exceedance
of any of the criteria, then the site was identified as requiring no further action. Regarding
groundwater or surface water protection.

- The site-specific results under the native vegetation recharge scenario were evaluated next to determine whether the site conditions resulted in exceedance of the groundwater or surface water protection criteria. If the site conditions did not cause an exceedance of any of the protection criteria under the native vegetation (no irrigation) recharge scenario, then the affected waste site was identified for application of institutional controls that will prevent irrigation in the future at the site.
- If the site-specific results under the native vegetation (no irrigation) recharge scenario indicated that the site conditions would result in an exceedance of any of the groundwater or surface water protection criteria, then the exceeding contaminants were identified as COCs for that site. In addition, the waste site was included in the FS for identification of appropriate remedial alternatives to mitigate risks to groundwater and surface water posed by the vadose zone contamination.

The assessment of vadose zone contaminant migration focused on evaluation of waste sites that have been characterized during the 100-D/H Area LFI, the current RI, or are sites at which planned soil remediation is complete and characterization describing the post-remediation conditions are available (that is, the "previously remediated sites"). In contrast, this assessment does not evaluate waste sites that are not yet remediated because these were carried directly forward into the FS for evaluation, with the COPCs identified based on process knowledge. The process followed for evaluation of previously remediated waste sites provided a basis for confirming the completion of the soil remediation at these sites. The same process was applied to the following 16 previously remediated sites located in 100-D/H using LFI, RI, and CVP/RSVP data:

- 116-D-1B Trench
- 116-D-7 Retention Basin
- 116-DR-1&2 Trench
- 116-DR-9 Retention Basin
- 116-H-1 Trench
- 116-H-4 Pluto Crib
- 116-H-6 Solar Evaporation Basin
- 116-H-7 Retention Basin
- 118-D-6:3 Reactor Fuel Storage Basin
- 118-H-6:2, 118-H-6:3, and 118-H-6:6 Reactor Fuel Storage Basin
- 100-D-12 French Drain
- 116-D-1A Trench
- 100-D-4 Trench
- 116-D-4 Crib
- 116-H-2 Trench/Crib
- 1607-H4 Septic System

Interim remedial action has continued, and vadose zone sampling was conducted at 142 of these interim-remediated waste sites, which were remediated per *Interim Remedial Action Record of Decision for the 100-BC-1, 100-DR-1, and 100-HR-1 Operable Units, Hanford Site, Benton County, Washington* (EPA/ROD/R10-95/126) through December 2012 (Table 5-1). CVP and/or RSVP data are available for the completed waste sites and evaluated through the risk assessment activities.

Table 5-1. Previously-Remediated Waste Sites in 100-D/H

	100-	100-H Area			
100-DR-1 OU	100-D-48:1	116-D-10	100-DR-2 OU	100-HR-1 OU	100-H-12
100-D-1	100-D-48:2	116-D-1A	100-D-12	100-H-17	100-H-14
100-D-18	100-D-48:3	116-D-2	100-D-13	100-H-21	118-H-6:3
100-D-19	100-D-48:4	116-D-4	100-D-15	100-H-24	118-H-6:6
100-D-2	100-D-49:2	116-D-5	100-D-28:1	100-H-28:1	118-H-6:5
100-D-20	100-D-49:3	116-D-6	100-D-43	100-H-28:6	118-H-6:4
100-D-21	100-D-49:4	116-D-7	100-D-47	100-H-3	1607-H2
100-D-22	100-D-50:5	116-D-9	100-D-94	100-H-35	1607-H3
100-D-24	100-D-52	116-DR-1 & 2	116-D-8	100-H-4	1607-H4
100-D-29	100-D-56:1	116-DR-5	116-DR-10	100-H-41	
100-D-3	100-D-56:2	116-DR-9	116-DR-4	100-H-45	<u>100-HR-2 OU</u>
100-D-31:1	100-D-61	118-D-6:4	116-DR-6	100-H-49:2	100-H-37
100-D-31:10	100-D-7	120-D-2	116-DR-7	100-H-5	100-H-40
100-D-31:2	100-D-70	126-D-2	116-DR-8	100-H-50	118-H-1:1
100-D-31:3	100-D-74	128-D-2	118-D-1	100-H-51:4	118-H-1:2
100-D-31:4	100-D-75:3	130-D-1	118-D-4	100-H-51:5	118-H-2
100-D-31:5	100-D-80:1	132-D-1	118-D-5	100-H-53	118-H-3
100-D-31:6	100-D-82	1607-D2:1	118-DR-1	100-H-7	118-H-4
100-D-31:7	100-D-83:4	1607-D2:2	118-DR-2:2	100-H-8	118-H-5
100-D-31:8	100-D-84:1	1607-D2:3	122-DR-1:2	116-H-1	128-H-I
100-D-31:9	100-D-85:1	1607-D2:4	1607-D1	116-H-3	128-H-2
100-D-32	100-D-87	1607-D4	600-30	116-H-5	128-H-3
100-D-4	100-D-88	1607-D5	ļ	116-H-7	1607-H1
100-D-42	100-D-9	628-3		116-H-9	600-151
100-D-45	100-D-90	UPR-100-D-5		100-H-11	600-152

# 5.2 Overview of the 100-D/H Conceptual Site Model

The CSM presented in Section 4.9 described how the operating history at 100-D/H contributed to sources of environmental contamination and presented how the primary sources related to secondary contamination sources and the integration of contaminant migration to known and potential receptor exposure points. Releases occurred during reactor operations. The retention basins are located between

the river and the coal plant. The water treatment operations are shown from the 182 Reservoir and the 183-D and 183-DR clearwells and head houses.

### 5.3 Contaminant Persistence

The persistence of various contaminants in the environment determines how long they are available for transport to different receptors. If a contaminant remains in the environment for a long time and is highly mobile ( $K_d = 0 \text{ mL/g}$ ), it is more likely to be transported from the vadose zone to groundwater and, eventually, to surface water. Persistence is defined by how long it takes a particular contaminant to be transformed into a less toxic or less available form, or how long it takes the contaminant to physically leave the affected area. Radionuclides undergo radioactive decay at varying rates specific to the individual nuclides. Nonradioactive chemicals may also degrade, decay, or undergo chemical transformation that reduces the residual mass of the contaminant available for transport or direct exposure. The following paragraphs discuss the persistence of the selected COPCs.

### 5.3.1 Persistence of Nonradioactive Chemical Constituents

The persistence of chemical constituents, and alternatively, the degradation of these compounds at 100-D/H is primarily driven by biological and geochemical reduction-oxidation processes, potential biological uptake, and physical processes (for example, volatilization and water solubility). The nonradioactive chemical constituents identified for this assessment include chromium measured as Cr(VI), which is generally present as a dissolved oxyanion or as a metallic salt, total chromium, which includes Cr(VI) and chromium in other valence states, zinc, other metals (e.g. copper, cadmium, and lead), nonmetallic oxyanions (nitrate and sulfate), and VOCs (carbon tetrachloride and chloroform). These constituents are subject to a variety of transformational processes. The processes that affect the persistence and mobility of metals present at 100-D/H are discussed in Section 4.5.12.

Both Cr(VI) and zinc are relatively stable and persistent in the vadose and groundwater environment at 100-D/H. Zinc is generally present as a divalent cation and does not undergo transformation under ambient conditions. Chromium is typically present in the environment in one of two oxidation states (trivalent or hexavalent). Trivalent chromium is typically precipitated as a low-solubility hydroxide molecule, Cr(OH)<sub>3</sub> and, as such, is not mobile and exhibits low mammalian toxicity. Cr(VI), however, is highly toxic and is typically present under ambient conditions at 100-D/H as a soluble oxyanion, Cr<sub>2</sub>O<sub>7</sub>-<sup>2</sup> or CrO<sub>4</sub>-<sup>2</sup>, depending primarily on pH (the dichromate oxyanion is dominant in acidic conditions; the chromate oxyanion is dominant in alkaline conditions). The ionic forms of Cr(VI) are relatively stable at the oxidation state typically found in soil and groundwater at 100-D/H, and the constituent tends to remain mobile.

While the largest primary source of Cr(VI) contamination in 100-D/H was sodium dichromate dihydrate used for corrosion control in reactor cooling water, another source is important to consider in evaluating groundwater data. Sodium dichromate is an acidic compound in its concentrated form. The dichromate, or chromate, ion can react with other metals in the environment to form compounds of lesser solubility. These compounds can include potassium dichromate (which is about one-tenth as soluble as sodium dichromate dihydrate) and lead chromate (which is essentially water insoluble). Cr(VI) ions can also be subject to chemical reduction under moderately reducing conditions, or by reaction with reducing agents such as ferrous iron. Ferrous iron is very effective at reducing Cr(VI) to Cr(III), producing a very low-solubility hydroxide molecule. Many of the metals of interest identified in soil and groundwater at 100-D/H are not considered very mobile with the exception of some species of chromium. Metals, such as zinc, arsenic, cadmium, and lead, are persistent in the environment but they are less mobile. However, chromium may be present in various oxidation and ionic states that affect the mobility in the environment. Cr(VI) is moderately mobile (0 mL/g <  $K_d \le 1$  mL/g) and toxic, whereas the reduced trivalent form

exhibits low mobility and is nontoxic. Mercury can be very mobile when it is in the presence of acid as may have been the case during reactor operations.

The mobility, and therefore persistence, of metals in vadose soil and within an aquifer system is influenced by several factors including: soil type, the cation exchange capacity of the soil (the ability to hold cations [that is, positively-charged ions] under a given condition), pH, and the presence of other metals. Cationic metals, such as  $^{90}\text{Sr}^{+2}$  tend to bind more easily to silt and clay particles in soil. This is a function of greater surface area being available for binding. In addition, the silt and clay fractions commonly exhibit a higher capacity for cation exchange and therefore for sorbing metal ions. Cation exchange is a substantial contributor to reduction in mobility of many metals in the vadose and aquifer system at 100-D/H.

Some metals (for example, arsenic and chromium) commonly exist in the environment as complex anions (for example, arsenate, arsenite, and chromate). These metal oxyanions are generally water-soluble and are not retained by soil particles to a large degree. Some soil particles (for example, organic matter and some clay minerals) do exhibit measureable anion exchange capacity under certain conditions of pH and reduction-oxidation potential. Anion exchange does not play a large role in limiting mobility of most oxyanions at 100-D/H.

Nitrate is a common plant nutrient and is a relatively stable oxyanion of nitrogen and oxygen. Its presence in groundwater beneath 100-D/H may be related to historical planned and unplanned releases of cooling water treatment chemicals, as well as from the use of nitric acid for various decontamination and cleaning activities in the reactors. Nitrate occurs in groundwater in proximity to the reactors and septic systems. It is highly water-soluble and remains stable in vadose zone soil and groundwater, and surface water under oxidizing conditions typically encountered at 100-D/H. Nitrate is subject to chemical or biological reduction to nitrite or ultimately to diatomic nitrogen by soil and water microorganisms under low-oxygen conditions. Reduction of nitrate to diatomic nitrogen generally results in removal of the nitrogen from the soil/water system. Nitrate is mobile, relatively stable, and persistent in groundwater.

Sulfate is a common plant nutrient, however, its presence in groundwater beneath 100-D/H may be related to historical planned and unplanned releases of cooling water treatment chemicals, as well as from the use of sulfuric acid for various decontamination and cleaning activities in the reactors. Sulfate is widespread with the highest concentrations observed downgradient of the ISRM reactive barrier. The sulfate at this location resulted from oxidation of the residual sulfhydryl (-SH) groups from the sodium dithionite reagent used to establish the ISRM barrier. Sulfate is mobile, relatively stable, and persistent in groundwater.

Carbon tetrachloride and chloroform will degrade very slowly, if at all, under typical dissolved oxygen concentrations in groundwater beneath 100-D/H. However, carbon tetrachloride and chloroform can be reductively dechlorinated by facultative<sup>1</sup> and obligate<sup>2</sup> anaerobic microorganisms under anoxic conditions. Additionally, carbon tetrachloride and chloroform may volatilize from the land surface or surface water directly to the atmosphere. Carbon tetrachloride and chloroform dissolved in soil moisture or groundwater can partition to soil gas and then migrate to the atmosphere; however, gas exchange from the deep vadose (for example, below a few meters below ground surface) or from groundwater accounts for only a tiny potential loss. Once in the atmosphere, these compounds can be destroyed through photolytic oxidation. The potential for volatilization or biologically mediated degradation is dependent

<sup>&</sup>lt;sup>1</sup> Can survive in both aerobic and anaerobic conditions.

<sup>&</sup>lt;sup>2</sup> Can survive only in anaerobic conditions.

upon the specific physical and chemical characteristics of a constituent and the size and nature of the microbial populations. The chlorinated solvents presented at 100-D/H are expected to be persistent in soil and groundwater.

### 5.3.2 Persistence of Radiological Constituents

Radiological constituent persistence is primarily controlled by radioactive decay processes that can transform the parent isotope into another isotope of the same element or into another element. The daughter product of decay may be a radionuclide or a stable isotope. Radionuclides with relatively high mobility and longer half-lives ( $T_{1/2}$ ) are of more environmental concern than radionuclides with lower mobility and shorter  $T_{1/2}$ . This is primarily due to the potential for constituents with higher mobility and longer half-lives to reach the saturated zone at higher activities and greater potential to migrate though groundwater. Chapter 6 identifies one radionuclide as a groundwater COPC (strontium-90). Strontium-90 is a beta particle-emitting fission product with a  $T_{1/2}$  of 28.8 years. The beta decay daughter product of strontium-90 is yttrium-90 ( $T_{1/2} = 64.1$  hours), which then beta decays to the stable zirconium-90 isotope. The radionuclides, their half-lives, and daughter products are further explained in *Composite Analysis for Low-Level Waste Disposal in the 200 Area Plateau of the Hanford Site* (PNNL-11800).

The persistence in groundwater of these nuclides is also affected by their individual unique chemical and physical behaviors. Strontium-90 commonly remains as an exchangeable divalent cation in the environment. As such, it is not highly mobile and tends to be retained on soil particles near its point of release. Retention of strontium on soil particles by cation exchange processes, however, is subject to competition by other common cations (for example, calcium). This competition can increase strontium mobility under some environmental conditions. This is a consideration with regard to the chemistry of dust suppression water and fixatives used in application/operation procedures.

# 5.4 Vadose Contaminant Migration Assessment

Concepts affecting contaminant transport in the vadose zone are presented in this section, followed by factors affecting contaminant transport in the saturated zone. Quantitative applications of these parameters and boundary conditions to develop analytical and numerical models of transport through the vadose and saturated zones are presented, with a discussion of each factor affecting contaminant migration. The results of the application of these models to develop groundwater and surface water protection comparison criteria (SSLs and PRGs) and predict future conditions are also presented.

Contaminants released from 100-D/H sources were transported through the vadose zone and, in some cases, reached the water table. This discussion focuses on factors affecting contaminant transport through the unsaturated and saturated zones of the unconsolidated matrix above the basalt. The most significant factors affecting ongoing subsurface contaminant migration are the type of surface cover and its effect on net infiltration or recharge rates; the physical, chemical, and hydraulic characteristics of the matrix; and the physical and chemical properties of the contaminant (Section 5.6.1).

Once contaminants reached groundwater, mobile contaminants traveled with groundwater in the general direction of flow. Contaminated groundwater can migrate downgradient to discharge directly into the adjacent Columbia River. Contaminated groundwater may also be seasonally discharged in springs or seeps to flow overland across the riparian zone to discharge into the river. Seasonal seep discharges may be a limited and localized source of recontamination of the ground surface in the riparian zone.

The assessment of vadose zone contaminant migration is focused on evaluation of waste sites that have been characterized during the 100-D/H LFI, the current RI, or are sites at which planned soil remediation is complete and characterization describing the post-remediation conditions are available (that is, the

"previously remediated sites"). Unremediated sites are elevated directly to the FS without undergoing the evaluation described here. This provides a basis for confirming the completion of the soil remediation at these sites. The same process was applied to 16 previously remediated sites located in 100-D/H using LFI, RI, and CVP/RSVP data.

Contaminant migration from 100-D/H waste sites through the vadose zone to the underlying aquifer is controlled by the driving forces, interactions between water and sediments, and interactions between the contaminants and sediments specific to the OUs. Driving forces include gravity; matric potential gradients; recharge, which is the result of competition between precipitation, evaporation, transpiration, infiltration, run-off, and run-on; and artificial discharges, such as those from septic tank leach fields, lagoons, pipe and tank leaks, and irrigation. The types, thicknesses, and properties of the sediments can all affect the rate and direction of solute and water movement to the aquifer. A contaminant's concentration in the groundwater and its concentration in the downgradient Columbia River, including the peak concentration, are dependent on the solute flux from the vadose zone; aquifer thickness, properties, and flux rates; travel distance; groundwater and river water mixing; and the location sampled. Each contaminant's decay rate (if applicable) and propensity to sorb to vadose zone or aquifer materials can also be important controlling factors on the peak concentration, from which the PRG or the screening level is calculated.

## 5.4.1 Surface Cover, Infiltration, and Recharge

The net infiltration into the vadose zone is driven by the competition between processes of precipitation (including snow), evaporation, transpiration, run-off, and run-on. In a semiarid or arid climate, downward fluxes resulting from this competition are episodic and usually infrequent. A number of studies have been carried out at the Hanford Site to ascertain representative long-term averages of the episodic fluxes (that is, recharge rates), such as those compiled in *Vadose Zone Hydrogeology Package for Hanford Site Assessments* (PNNL-14702), hereinafter called Vadose Zone Hydrogeology Package, for the 100 Area. The 100 Area-specific recharge rates in the Vadose Zone Hydrogeology Package (PNNL-14702) varied with surface soil type and provided an estimate of the range of possible recharge rates for various land uses. The four surface soil types identified in the 100 Area were the Ephrata Sandy Loam, Ephrata Stony Loam, Burbank Loamy Sand, and Rupert Sand. However, recharge rates for the Ephrata Sandy Loam and the Ephrata Stony Loam were described as being identical (Vadose Zone Hydrogeology Package [PNNL-14702]). Additionally, the Vadose Zone Hydrogeology Package (PNNL-14702) also provides recharge rates for disturbed soil conditions: the disturbed soil rates were selected for use in calculation of SSLs and PRGs for the 100-D and 100-H source OUs.

The long-term natural driving force for flow and transport through the vadose zone is the downward movement of water. This movement is expressed as follows (*Compendium of Data for the Hanford Site (Fiscal Years 2004 to 2008) Applicable to Estimation of Recharge Rates* [PNNL-17841]):

- Infiltration refers to water usually resulting from precipitation that enters the ground. Enhanced infiltration may result where surface depressions act as terminuses for overland flow.
- Deep percolation or deep drainage refers to water that has percolated or drained below the zone of evaporation and the influence of plant roots.
- Recharge is water that flows to the water table, and is the primary mechanism for transporting contaminants from the vadose zone to groundwater.

Direct measurement of naturally occurring recharge resulting from surface infiltration at the Hanford Site is not practical. The measurement is made indirectly because of the thickness of the vadose zone and the time necessary for water to travel from the land surface to the water table. In place of direct

measurements of recharge at the water table, measurements and analyses of deep drainage in the unsaturated zone are used to approximate the recharge. The terms can be equated, as long as the climate, land use, and land cover remain the same. Consequently, the terms "deep percolation" or "deep drainage" are often used synonymously with recharge.

There is ample evidence that revegetation of the disturbed land at the Hanford Site occurs both with and without human intervention. Data collected from the Prototype Hanford Barrier in 200 East Area indicate the tall sagebrush (*Artemisia tridentata*) community begins to reduce net infiltration very soon after planting. The species richness of the plant community on the Prototype Hanford Barrier dropped from 35 in 1997 to 12 in 2007. The dominance of tall sagebrush on the surface may continue to reduce the species richness on the surface (Figure 5-2).



Source: Figure 4.1 from PNNL-17176, 200-BP-1 Prototype Hanford Barrier Annual Monitoring Report for Fiscal Years 2005 Through 2007.

Figure 5-2. Prototype Hanford Barrier Cover in 2007 Dominated by Sagebrush (*Artemisia tridentata*), 13 Years after Plant Community Establishment

Grass cover has decreased from initial levels on the barrier surface, and continued decreasing from 2004 to 2007. Cheatgrass (*Bromus tectorum*) and Russian thistle (*Salsola kali*) are nearly nonexistent on the barrier surface. The western and northern side slopes of the barrier, which were not planted with sagebrush, show less plant cover but higher species diversity than the barrier surface. This may be due to the influence of windblown material and seeds from adjacent land, or the lack of shrubs competing for resources. Insects and small mammals are present in the barrier surface, which indicates the restored barrier surface is beginning to function like a recovering ecosystem.

Numerous studies have estimated recharge rates for the vadose zone system at the Hanford Site under various surface cover conditions. One such study (*Estimated Recharge Rates at the Hanford Site* [PNL-10285]) cites the results of radioisotopic tracer studies that were used to estimate recharge rates under various covers. This included an evaluation of the Ephrata Sandy Loam and Ephrata Stony Loam soil types present at 100-D/H, where the chlorine-36 tracer study indicated a recharge rate of 2.6 mm/yr under shrub and bunchgrass cover. The same report describes estimated recharge rates of 4.9 mm/yr and 17.3 mm/yr for cheatgrass and bare ground, respectively.

The recharge rate affects the velocity of pore water through the vadose zone. The flow velocity in the vadose zone is expected to have been greatest beneath the ponds, French drains, trenches, and cribs during the operational periods when percolation was at its greatest. A similar increase would have occurred in the vadose zone beneath unlined ditches. The velocity of downward movement is expected to have decreased after the waste disposal ceased, as the subsurface water content profile began to equilibrate to new surface conditions. After the waste disposal operations ended, alterations to the surface cover (including excavation of contaminated soil, backfilling the excavation with clean fill, revegetation, and stabilization) began to alter the net infiltration rate into the vadose zone.

The recharge input values to the Subsurface Transport Over Multiple Phases (STOMP) models for the SSL calculation (based on irrigated agriculture land use) and the PRG calculation (based on conservation land use) were obtained from the vadose zone data package compiled in the Vadose Zone Hydrogeology Package (PNNL-14702). These data provided the basis for stipulating recharge rates in the two sequential models used to derive SSLs and PRGs. The first simulation, called the historic (pre-2010 model) and using recharge rates for the historic phases listed in Tables 5-2 and 5-3, was used to establish the initial matric potential distribution in the vadose zone for subsequent modeling in the predictive (post-2010) model. Two different scenarios based on future land use were evaluated in the predictive (post-2010) simulations that simulated the migration of water and contaminants to the underlying aquifer using recharge rates for two recharge scenarios for future conditions shown in Table 5-2 (native vegetation recharge scenario) and Table 5-3 (irrigation recharge scenario). Summarized in the following paragraphs, the recharge scenarios and rates are discussed in detail in STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units (ECF-HANFORD-11-0063) in Appendix F.

Table 5-2. Native Vegetation Recharge Scenario Phases and Recharge Rates (mm/yr)

	Historic Simulation (pre-2010) (calculation of initial hydraulic conditions)			Predictive Simulation (post-2010) (calculation of peak groundwater concentration)			
Surface Soil Type	Pre-Settlement (< 1880)	Historic Irrigation <sup>a</sup> (1880-1944)	Hanford Operations (1944-2010)	Bare Soil (2010-2015)	Cheatgrass (2015-2020)	Developing Shrub-Steppe (2020-2050)	Mature Shrub-Steppe (2050 >)
Hanford sand, disturbed	4.0 <sup>b</sup>	72.4°	63.0 <sup>d</sup>	63.0 <sup>d</sup>	31.5°	$8.0^{\rm f}$	4.0 <sup>g</sup>

a. Irrigated agriculture was prevalent in the 100-D/H Area prior to Hanford Site construction; irrigation therefore was conservatively assumed applicable to all 100-D/H sites from calendar years 1880 through 1944.

- d. Source: PNNL-14702 (Table 4-15), all areas with soils disturbed by excavations; no vegetation.
- e. Source: PNNL-14702 (Table 4-15), all areas with soils disturbed by excavations; cheatgrass.
- f. Source: PNNL-14702 (Table 4-15), all areas with soils disturbed by excavations; young shrub steppe.
- g. Source: PNNL-14702 (Table 4-15), all areas with soils disturbed by excavations; shrub steppe.

b. Source: PNNL-14702, Vadose Zone Hydrogeology Package for Hanford Site Assessments (Table 4-15), all areas with soils disturbed by excavations; shrub steppe.

c. Recharge rates for historic irrigation phase is that from the long-term irrigation rate (Irrigation II) under the irrigation recharge scenario (Table 5-3).

For the historic (pre-2010) simulations, land use and recharge rates were assumed to transition from native vegetation (mature shrub-steppe) during pre-settlement conditions, to a historic irrigation period for 1880 to 1944, to a Hanford Site operational period with bare soil from 1944 to 2010. The pre-settlement phase was assumed to begin in calendar year 0, an arbitrary date that was selected merely to ensure steady-state moisture conditions are achieved in the solution for the applicable recharge rate by the 1880 year of transition to historic irrigation (1880). Historic irrigation is included in the historic period because multiple land areas in the 100-D and 100-H area were used for irrigated agriculture prior to construction of the Hanford Site. The historic irrigation period is assumed to commence in 1880, and is further assumed applicable to all waste sites in the 100-D and 100-H source OUs. The Hanford Site operational period is assumed to consist of bare soil conditions, maintained vegetation free, for all waste sites. The recharge rates for each historic phase (pre-settlement with native vegetation, historic irrigation, Hanford operations) are applied to the top boundary as a constant rate within each phase.

The first recharge scenario simulated in the predictive model is based on conservation land use and termed as the native vegetation recharge scenario, included the maturation of shrub-steppe in four phases starting from bare soil, transitioning to cheatgrass, then to mixed grass and shrub cover, and finally to mature shrub-steppe cover (Table 5-2). The second recharge scenario, termed the irrigation recharge scenario (Table 5-3), included the same bare soil period as for the native vegetation scenario followed by application of irrigation recharge rates that were represented by infiltration increments over the corresponding native vegetation rate (from Table 5-2) (per WDOH/320-015, *Hanford Guidance for Radiological Cleanup*). Recharge for native vegetation is a function of both the surface soil type and the kind and extent of vegetation cover. Recharge rates for disturbed soil conditions were taken from the Vadose Zone Hydrogeology Package (PNNL-14702, Section 4.5). Recharge rates for each scenario were determined using the rates for the disturbed soil type and vegetation cover conditions. Rates were assumed to change over time in step function fashion for the two scenarios in the predictive period.

Table 5-3. Irrigation Recharge Scenario Phases and Recharge Rates (mm/yr)

	Historic Simulation (pre-2010) (Calculation of Initial Hydraulic Conditions)			Predictive Simulation (post-2010) (Calculation of Peak Groundwater Concentration)			
Surface Soil Type	Pre-Settlement (<1880)	Historic Irrigation <sup>a</sup> (1880-1944)	Hanford Operations (1944-2010)	Bare Soil (2010-2015)	Irrigation I (2015-2045)	Irrigation II (2045>)	
Hanford sand, disturbed	4.0 <sup>b</sup>	72.4°	63.0 <sup>d</sup>	63.0 <sup>d</sup>	76.4 <sup>e</sup>	72.4 <sup>e</sup>	

a. Irrigated agriculture was prevalent in the 100-D/H Area prior to Hanford Site construction; irrigation therefore was conservatively assumed applicable to all 100-D/H sites from calendar years 1880 through 1944.

Three recharge periods were specified in the predictive (post-2010) simulations to represent changes in recharge rates following the assumed future land use of each recharge scenario (Tables 5-2 and 5-3).

b. Source: PNNL-14702, Vadose Zone Hydrogeology Package for Hanford Site Assessments (Table 4-15), all areas with soils disturbed by excavations; shrub steppe.

c. Recharge rates for historic irrigation phase is that from the long-term irrigation rate (Irrigation II phase).

d. Source: PNNL-14702 (Table 4-15), all areas with soils disturbed by excavations; no vegetation.

e. Recharge rates for future irrigation phases represent incremental increases over corresponding undisturbed native vegetation recharge rates, based on WDOH/320-015, *Hanford Guidance for Radiological Cleanup*. The recharge increment attributable to irrigation alone is 68.4 mm/yr. This increment is added to the corresponding rate for immature shrub steppe (8.0 mm/yr) and mature shrub steppe (4.0 mm/yr) phases of the native vegetation recharge scenario (Table 5-2) to obtain the total recharge rate.

For both scenarios, bare soil was assumed to continue to be the land cover above the waste site during the first recharge period, from 2010 to 2015.

For the native vegetation recharge scenario, the third predictive recharge phase is 30 years in duration based on transition period duration information in Regulatory Basis and Implementation of a Graded Approach to Evaluation of Groundwater Protection (DOE/RL-2011-50), and represents grasses and shrubs covering bare soil. The fourth predictive recharge phase represents the establishment of a mature shrub-steppe that continues for the remainder of the predictive simulation. Thus, recharge rates decreases with time in this native vegetation recharge scenario as the vegetation cover transitions from bare soil towards a mature shrub-steppe state that is maintained thereafter (Table 5-2). Revegetation of waste sites following remediation is assumed in this scenario, consistent with revegetation that is occurring in the 100 Areas accordance with BRMaP (DOE/RL-96-32). Revegetation has been successfully conducted in the 100 Area following other remediation activities; for examples, refer to the annual River Corridor Closure Contractor Revegetation and Mitigation Monitoring Reports, including 2008 River Corridor Closure Contractor Revegetation and Mitigation Monitoring Report (WCH-288), 2008 River Corridor Closure Contractor Revegetation and Mitigation Monitoring Report (WCH-362), 2010 River Corridor Closure Contractor Revegetation and Mitigation Monitoring Report (WCH-428), 2011 River Corridor Closure Contractor Revegetation and Mitigation Monitoring Report (WCH-512), and 2012 River Corridor Closure Contractor Revegetation and Mitigation Monitoring Report (WCH-554).

Recharge rates for the irrigation recharge scenario were estimated using the same approach employed to assess interim remediation at 100 Area waste sites (100 Area RDR/RAWP [DOE/RL-96-17]). Recharge rates for the irrigation scenario were estimated using the same parameters employed to assess interim remediation at 100 Area waste sites. These site assessments used irrigation infiltration rates calculated from an overall 0.76 m/yr (30 in/yr) irrigation rate and an evapotranspiration coefficient value of 0.91 (WDOH/320-015, Appendix B). The resultant recharge rate attributable to irrigation alone [68.4 mm/yr (2.7 in/yr) was added to the native vegetation recharge rates for the corresponding phase to determine a summed recharge rate (total) for the irrigation scenario for each soil type in the SSL and PRG estimate simulations. The resulting recharge rates for native vegetation and irrigation recharge scenarios are shown in Table 5-3.

For the SSL calculation, the maximum foreseeable recharge scenario (irrigation) was applied for each surface soil type (Table 5-3) at 100-D/H. For the PRG value calculation, the reasonably anticipated land use scenario (conservation with native vegetation) was applied for each surface soil type (Table 5-3).

# 5.4.2 Stratigraphy

The characteristics of material in the vadose zone affecting contaminant mobility are the particle size, permeability, and organic content of the lithologies present beneath the waste site. The primary mechanism for transport in the vadose zone is the flow of infiltrating water in response to gravitational and capillary forces. The pore networks (represented by grain-size distributions in each vertical lithologic sequence, the hydraulic and transport properties of each lithologic unit in the sequence, and the thickness of each lithologic unit) affect water flow and contaminant transport through the vadose zone. The unsaturated hydraulic conductivity of each lithologic unit varies with moisture content and, therefore, is a function of matric potential. The effects of the different lithologic units and variations in their individual thicknesses in 100-D/H on screening level and PRG values were determined by running STOMP simulations for a number of stratigraphic columns that represented the range of variations in 100-D/H.

The Hanford formation, Ringold Formation unit E, and the RUM were described in Chapter 3 (Section 3.4). Borehole data were used to identify representative stratigraphic columns for 100-D and

100-H. Two lithologic units are present in the 100-D vadose zone: the gravel-dominated Hanford formation and the Ringold Formation unit E. Only the Hanford formation is present in 100-H vadose zone. Because of its coarse texture and higher hydraulic conductivity, the Hanford formation transmits water and dissolved or suspended contaminants more rapidly than the underlying Ringold Formation unit E does.

The contact between the Hanford formation and the Ringold Formation unit E forms a textural discontinuity that can result in temporary perching of water atop the interface during saturated vertical flow conditions in the vadose zone. During historical high-volume water discharges, a substantial quantity of water carrying dissolved Cr(VI) and other contaminants was transmitted vertically and laterally through the Hanford formation to locations considerably distant from the points of release. This was particularly notable at the 116-DR-1&2 Trench, where a substantial groundwater mound formed in the Hanford formation beneath the trench, and extended for thousands of meters inland both upstream and downstream, and across the Horn. The variability in stratigraphy observed at 100-D/H was recognized during design of the vadose transport simulation model used to evaluate the potential for migration of contaminants from the vadose zone to groundwater. The representative stratigraphic columns shown in Figures 5-3 and 5-4 illustrate how the variability was integrated into the transport simulations.

The water table elevations of June 2008 were selected to provide representative (not extreme) high water table conditions; the month of June is typically when the highest river stage occurs annually in this reach of the Columbia River. Use of water table elevations from the high water stage period (represented by June 2008 data) result in a smaller thickness of the vadose zone for each well and borehole to develop the representative stratigraphic profiles. Biasing these columns toward smaller vadose zone extents minimizes transport distance and time, thereby biasing peak groundwater concentrations to earlier arrival times and higher magnitudes than would be the case for mean thicknesses. These well and borehole data were used to estimate the thickness of each lithologic unit within the vadose zone and within the unconfined aquifer. These wells and boreholes were divided into groups based on the proportion of each lithologic unit and total vadose zone thickness. A representative stratigraphic column was selected for each well and borehole group, resulting in six stratigraphic columns for 100-D (Figure 5-3) and two stratigraphic columns for 100-H (Figure 5-4) to support model construction for the STOMP simulations, Each column was assumed to contain clean backfill to represent conditions following interim remediation. Clean backfill was assumed to replace the uppermost 4.5 m (15 ft) of each column. Additional details regarding the development of these stratigraphic columns, including sensitivity studies on the backfill thickness representation that demonstrate it is an insensitive parameter, are presented in STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units (ECF-HANFORD-11-0063) in Appendix F.

### 5.4.3 Sorption

Mobility of constituents can be characterized using the soil/water  $K_d$ . This parameter is dependent upon the geochemical characteristics of the constituent, the properties of the transporting water, and the nature of the soil matrix. In general, organic constituents with lower molecular weights have lower  $K_d$  values than those with higher molecular weights. The  $K_d$  values of metallic radionuclides and nonradiological metals are primarily influenced by the charge sign (positive or negative) and magnitude of charge of the dominant species in a given geochemical environment (that is, positively charged ions tend to become attached to the negatively charged soil particles, while negatively charged ions tend to be repelled from soil particles and remain in solution).

Tritium is often used as a tracer for water molecules in column breakthrough testing and is assumed to define the zero  $K_d$  condition. It is conceivable that tritium substituted for hydrogen in a water molecule or hydroxyl species can exchange with water molecules adsorbed to solids or with hydroxyl groups on the

surfaces of solid hydrous oxides ( $K_d$  Values for Agricultural and Surface Soils for Use in Hanford Site Farm, Residential, and River Shoreline Scenarios: Technical Report for Groundwater Protection Project—Characterization of Systems Task [PNNL-16531]).

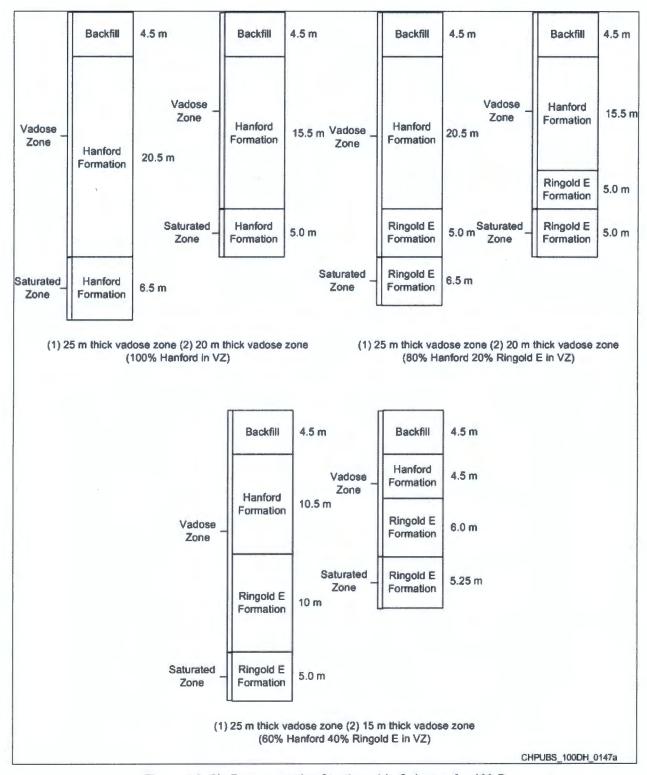


Figure 5-3. Six Representative Stratigraphic Columns for 100-D

Several metals of environmental concern exist in vadose zone material in more than one oxidation state: trivalent and pentavalent arsenic and trivalent and hexavalent chromium. The oxidation state and mineral speciation of these metals determines their relative mobility. Cr(VI), originally released as high-solubility sodium dichromate dihydrate, is relatively mobile in solution, being only weakly sorbed. Cr(VI); however, for other mineral compounds and a fraction of soil residues, it may be present in soil as relatively low-solubility mineral species such as potassium dichromate or lead chromate. Alternatively, Cr(III) is relatively immobile ( $K_d > 30 \text{ mL/g}$ ), being generally present as relatively insoluble precipitates, such as chromic hydroxide,  $Cr(OH)_3$  (*Behavior of Metals in Soils* [EPA/540/S-92/018]).

Cr(VI) is a predominantly anionic species in the oxygenated, neutral to slightly basic pH pore water and groundwater observed in the subsurface at 100-D/H. Anionic species typically have relatively low  $K_d$  values and are considered to exhibit high to slight mobility in the 100-D/H subsurface environment. Cr(VI) may exist as the chromate ions  $HCrO_4^-$  (predominant at pH <6.5) or  $CrO_4^{-2}$  (predominant at pH 6.5) and as the dichromate ion  $Cr_2O_7^{-2}$  (predominant at concentrations >10 mM and at pH 2-6). In low ionic strength solutions, only the hexavalent chromate anion,  $CrO_4^{-2}$ , is found in oxidizing and near-neutral pH conditions.

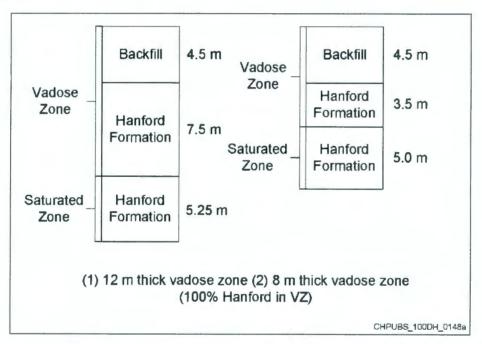


Figure 5-4. Two Representative Stratigraphic Columns for 100-H

Strontium-90 and uranium are most likely to exist as cationic species in the 100-D/H subsurface environment. Cationic species, which have higher  $K_d$  values than the anions, are typically considered moderately mobile (0 mL/g <  $K_d \le 1$  mL/g) to essentially immobile ( $K_d > 30$  mL/g). Cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption is pH dependent, increasing with increasing pH. Strontium-90 and uranium may become immobilized by forming precipitates with phosphate, carbonate, and hydroxide (*Behavior of Metals in Soils* [EPA/540/S-92/018]).

Table 5-4 summarizes the mobility of these contaminants. These contaminants are grouped by their relative mobility and the  $K_d$  values. Contaminants in the slight mobility group exhibit a high degree of interaction with vadose zone and aquifer solids and, as a result, migrate slowly through the vadose zone and aquifer. Their concentration in the vadose zone decreases rapidly with increasing depth, and their dissolved concentration in groundwater decreases dramatically with distance from a source or release

point. The decrease in concentration is due to the relatively large fraction of the contaminant that interacts with, and become sorbed to, the solid materials in the vadose zone and aquifer. For this discussion and comparison, the slight mobility group includes contaminants that exhibit  $K_d$  values greater than 1 but less than 30 mL/g.

**Inorganics** Radionuclides **Organics** Nitrate Tritium None Sulfate Increasing rate of Migration Carbon Tetrachloride Hexavalent Chromium None Moderate Chloroform ncreasing interaction with soil sumed K<sub>d</sub> Value for Mobility Increasing K<sub>d</sub> Sr-90 None Arsenic Slight Zinc Am-241 None Chromium (Cr+3) Cs-137 mmobile Pu-238 Pu-239/240 Co-60 Ni-63 Eu-152 Eu-154 CHSGW20140333

Table 5-4. Mobility of 100-D/H Contaminants of Potential Concern

Contaminants considered essentially immobile ( $K_d > 30 \text{ mL/g}$ ) sorb so strongly to vadose zone material that no migration is observed with infiltrating water under near-neutral pH in the vadose zone. Liquid waste sources with highly acidic or basic pH values or those that contained complexing agents may have transported these contaminants into the vadose zone at the time of disposal, but migration decreased as the liquid waste equilibrated with the vadose zone material. These constituents are not expected to reach the unconfined aquifer except at waste sites with subsurface release mechanisms and a very thin vadose zone. Those that may have reached the unconfined aquifer are not expected to migrate further through the aquifer. The low mobility contaminants are identified as those that exhibit  $K_d$  values greater than 30 mL/g, for comparison purposes.

The  $K_d$  values used for the STOMP simulations were selected in *Groundwater and Surface Water Cleanup Levels and Distribution Coefficients for Nonradiological and Radiological Analytes in the 100 Areas and 300 Area* (ECF-HANFORD-12-0023), in Appendix F. The process followed to select  $K_d$  values was as follows: distribution coefficients ( $K_d$ ) values and soil organic carbon-water partitioning coefficient ( $K_{oc}$ ) values are obtained from a hierarchy of sources for each analyte evaluated. The specific steps used to compile the  $K_d$  values are as follows:

- 1. Identify analyte-specific  $K_d$  values or  $K_{oc}$  values from the following hierarchy of sources:
  - a. Ecology, 2014, "Cleanup Levels and Risk Calculations (CLARC)" database, Washington State Department of Ecology, available at: https://fortress.wa.gov/ecy/clarc/.

- b. EPA, 2012, "Regional Screening Levels for Chemical Contaminants at Superfund Sites," U.S. Environmental Protection Agency, updated November, 2012, available at: http://www.epa.gov/reg3hscd/risk/human/rb-concentration\_table/.
- c. ORNL, 2014, "Risk Assessment Information System," Oak Ridge National Laboratory, available at: http://rais.ornl.gov/.
- For organic analytes, identify analyte-specific soil organic carbon-water partitioning coefficients (K<sub>oc</sub>) and calculate a K<sub>d</sub> value using Equation 747-2 from WAC 173-340-747, "Deriving Soil Concentrations for Groundwater Protection," as follows:

$$K_d = K_{oc} \times f_{oc}$$

where:

 $K_d$  = distribution coefficient (mL/g)

 $K_{oc}$  = soil organic carbon-water partitioning coefficient (analyte-specific) (mL/g)

 $f_{oc}$  = soil fraction of organic carbon (0.001) (g/g)

- 3. For radiological target analytes, K<sub>d</sub> values are obtained from DOE/RL-96-17.
- 4. Exception: the selected Kd value for hexavalent chromium is 0.8 mL/g. This value is obtained from Evaluation of Hexavalent Chromium Leach Test Data Conducted on Vadose Zone Sediment Samples from the 100 Area (ECF-HANFORD-11-0165), providing a site-specific conservative value to represent the mobility of the residual fraction of Cr(VI) remaining in the soil column following remediation of a waste site. (Note this is not representative of the mobility of the mobile fraction of Cr(VI) that has migrated to groundwater prior to remediation.)
- Exception: the selected Kd value for total petroleum hydrocarbons is 4.0 mL/g. This value is obtained from Saturated Zone Flow and Transport Modeling in Support of 100-N RI/FS Document (ECF-100NR2-12-0053).

The values resulting from this process that were used to simulate each COPC with STOMP are listed in Table 5-5 for nonradiological COPCs and in Table 5-6 for radiological COPCs.

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (K₀) in Ascending Mobility Order

CAS#	Constituent Name	Selected K <sub>d</sub> (mL/g)	Source of Selected K <sub>d</sub> <sup>a</sup>
16887-00-6	Chloride	0	EPA, 2012
14797-55-8	Nitrate	0	EPA, 2012
14797-65-0	Nitrite	0	EPA, 2012
NO3-N	Nitrogen in Nitrate	0	EPA, 2012
NO2-N	Nitrogen in Nitrite	0	EPA, 2012
NO2+NO3-N	Nitrogen in Nitrite and Nitrate	0	EPA, 2012
14808-79-8	Sulfate	0	EPA, 2012
18496-25-8	Sulfide	0	EPA, 2012
51-28-5	2,4-Dinitrophenol	1.00E-05	CLARC, 2014

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (K<sub>d</sub>) in Ascending Mobility Order

CAS#	Constituent Name	Selected K <sub>d</sub> (mL/g)	Source of Selected K <sub>d</sub> <sup>n</sup>	
67-64-1	Acetone	5.75E-04	CLARC, 2014	
107-21-1	Ethylene glycol	0.0010	EPA, 2012	
67-56-1	Methanol	0.0010	EPA, 2012	
111-76-2	2-Butoxyethanol	0.0028	EPA, 2012	
75-99-0	Dalapon	0.0032	EPA, 2012	
78-93-3	2-Butanone	0.0045	EPA, 2012	
141-78-6	Ethyl acetate	0.0056	EPA, 2012	
79-06-1	Acrylamide	0.0057	EPA, 2012	
74-87-3	Chloromethane	0.0060	CLARC, 2014	
107-13-1	Acrylonitrile	0.0085	EPA, 2012	
74-83-9	Bromomethane	0.0090	CLARC, 2014	
60-29-7	Diethyl ether	0.0097	EPA, 2012	
75-09-2	Methylene chloride	0.010	CLARC, 2014	
108-10-1	4-Methyl-2-pentanone	0.013	EPA, 2012	
111-91-1	Bis(2-Chloroethoxy)methane	0.014	EPA, 2012	
591-78-6	2-Hexanone	0.015	EPA, 2012	
75-01-4	Vinyl chloride	0.019	CLARC, 2014	
75-00-3	Chloroethane	0.022	EPA, 2012	
621-64-7	n-Nitrosodi-n-dipropylamine	0.024	CLARC, 2014	
10061-01-5	cis-1,3-Dichloropropene	0.027	CLARC, 2014	
10061-02-6	trans-1,3-Dichloropropene	0.027	CLARC, 2014	
1918-00-9	Dicamba	0.029	EPA, 2012	
108-95-2	Phenol	0.029	CLARC, 2014	
94-75-7	2,4-Dichlorophenoxyacetic acid	0.030	EPA, 2012	
131-11-3	Dimethyl phthalate	0.032	ORNL, 2014	
156-59-2	cis-1,2-Dichloroethylene	0.036	CLARC, 2014	
107-06-2	1,2-Dichloroethane	0.038	CLARC, 2014	
156-60-5	trans-1,2-Dichloroethylene	0.038	CLARC, 2014	
1918-02-1	4-Amino-3,5,6-trichloropicolinic acid	0.039	EPA, 2012	
540-59-0	1,2-Dichloroethene (Total)	0.040	EPA, 2012	
75-69-4	Trichloromonofluoromethane	0.044	EPA, 2012	
75-15-0	Carbon disulfide	0.046	CLARC, 2014	

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (K<sub>d</sub>) in Ascending Mobility Order

CAS#	Constituent Name	Selected K <sub>d</sub> (mL/g)	Source of Selected K <sub>d</sub> <sup>a</sup>	
78-87-5	1,2-Dichloropropane	0.047	CLARC, 2014	
78-59-1	Isophorone	0.047	CLARC, 2014	
93-65-2	2-(2-methyl-4-chlorophenoxy) propionic acid	0.049	EPA, 2012	
120-36-5	Dichloroprop	0.049	ORNL, 2014	
75-34-3	1,1-Dichloroethane	0.053	CLARC, 2014	
67-66-3	Chloroform	0.053	CLARC, 2014	
75-27-4	Bromodichloromethane	0.055	CLARC, 2014	
71-43-2	Benzene	0.062	CLARC, 2014	
124-48-1	Dibromochloromethane	0.063	CLARC, 2014	
75-35-4	1,1-Dichloroethene	0.065	CLARC, 2014	
106-47-8	4-Chloroaniline	0.066	CLARC, 2014	
606-20-2	2,6-Dinitrotoluene	0.069	CLARC, 2014	
79-00-5	1,1,2-Trichloroethane	0.075	CLARC, 2014	
111-44-4	Bis(2-chloroethyl) ether	0.076	CLARC, 2014	
79-34-5	1,1,2,2-Tetrachloroethane	0.079	CLARC, 2014	
84-66-2	Diethylphthalate	0.082	CLARC, 2014	
108-60-1	Bis(2-chloro-1-methylethyl)ether	0.083	EPA, 2012	
95-48-7	2-Methylphenol (cresol, o-)	0.091	CLARC, 2014	
79-01-6	Trichloroethene	0.094	CLARC, 2014	
121-14-2	2,4-Dinitrotoluene	0.096	CLARC, 2014	
94-82-6	2,4-DB(4-(2,4-Dichlorophenoxy)butanoic acid)	0.098	EPA, 2012	
93-76-5	2,4,5-T(2,4,5-Trichlorophenoxyacetic acid)	0.11	EPA, 2012	
88-74-4	2-Nitroaniline	0.11	EPA, 2012	
99-09-2	3-Nitroaniline	0.11	ORNL, 2014	
100-01-6	4-Nitroaniline	0.11	EPA, 2012	
98-95-3	Nitrobenzene	0.12	CLARC, 2014	
75-25-2	Bromoform	0.13	CLARC, 2014	
71-55-6	1,1,1-Trichloroethane	0.14	CLARC, 2014	
108-88-3	Toluene	0.14	CLARC, 2014	
120-83-2	2,4-Dichlorophenol	0.15	CLARC, 2014	
56-23-5	Carbon tetrachloride	0.15	CLARC, 2014	
93-72-1	2,4,5-TP(2-(2,4,5-Trichlorophenoxy)propionic acid)Silvex	0.18	EPA, 2012	

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (K<sub>d</sub>) in Ascending Mobility Order

CAS#	Constituent Name	Selected K <sub>d</sub> (mL/g)	Source of Selected K <sub>d</sub> <sup>2</sup>	
100-41-4	Ethylbenzene	0.20	CLARC, 2014	
108-38-3	m-Xylene	0.20	CLARC, 2014	
105-67-9	2,4-Dimethylphenol	0.21	CLARC, 2014	
108-90-7	Chlorobenzene	0.22	CLARC, 2014	
1330-20-7	Xylenes (total)	0.23	CLARC, 2014	
95-47-6	o-Xylene	0.24	CLARC, 2014	
127-18-4	Tetrachloroethene	0.27	CLARC, 2014	
100-02-7	4-Nitrophenol	0.29	ORNL, 2014	
88-75-5	2-Nitrophenol	0.30	ORNL, 2014	
106-44-5	4-Methylphenol (cresol, p-)	0.30	EPA, 2012	
95-50-1	1,2-Dichlorobenzene	0.38	CLARC, 2014	
541-73-1	1,3-Dichlorobenzene	0.38	ORNL, 2014	
88-06-2	2,4,6-Trichlorophenol	0.38	CLARC, 2014	
95-57-8	2-Chlorophenol	0.39	CLARC, 2014	
59-50-7	4-Chloro-3-methylphenol	0.49	EPA, 2012	
87-86-5	Pentachlorophenol	0.59	CLARC, 2014	
106-46-7	1,4-Dichlorobenzene	0.62	CLARC, 2014	
98-82-8	Isopropylbenzene	0.70	EPA, 2012	
91-94-1	3,3'-Dichlorobenzidine	0.72	CLARC, 2014	
534-52-1	4,6-Dinitro-2-methylphenol	0.75	EPA, 2012	
18540-29-9	Hexavalent Chromium	0.80	ECF-Hanford-11-0165	
100-42-5	Styrene	0.91	CLARC, 2014	
91-20-3	Naphthalene	1.2	CLARC, 2014	
86-30-6	n-Nitrosodiphenylamine	1.3	CLARC, 2014	
58-89-9	Gamma-BHC (Lindane)	1.4	CLARC, 2014	
95-95-4	2,4,5-Trichlorophenol	1.6	CLARC, 2014	
84-74-2	Di-n-butylphthalate	1.6	CLARC, 2014	
120-82-1	1,2,4-Trichlorobenzene	1.7	CLARC, 2014	
319-84-6	Alpha-BHC	1.8	CLARC, 2014	
67-72-1	Hexachloroethane	1.8	CLARC, 2014	
959-98-8	Endosulfan I	2.0	CLARC, 2014	
319-85-7	beta-1,2,3,4,5,6-Hexachlorocyclohexane (beta-BHC)	2.1	CLARC, 2014	

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (K<sub>d</sub>) in Ascending Mobility Order

CAS#	Constituent Name	Selected K <sub>4</sub> (mL/g)	Source of Selected K <sub>d</sub> <sup>a</sup>	
126-73-8	Tributyl phosphate	2.4	EPA, 2012	
91-58-7	2-Chloronaphthalene	2.5	EPA, 2012	
91-57-6	2-Methylnaphthalene	2.5	EPA, 2012	
319-86-8	Delta-BHC	2.8	ORNL, 2014	
7440-42-8	Boron	3.0	EPA, 2012 <sup>b</sup>	
101-55-3	4-Bromophenylphenyl ether	3.1	ORNL, 2014	
7005-72-3	4-Chlorophenylphenyl ether	3.1	ORNL, 2014	
7421-93-4	Endrin aldehyde	3.3	ORNL, 2014	
86-74-8	Carbazole	3.4	CLARC, 2014	
7723-14-0	Phosphorus	3.5	EPA, 2012	
PO4-P	Phosphorus in phosphate	3.5	EPA, 2012	
TPH	Total petroleum hydrocarbons	4	ECF-100NR2-0053	
TPHDIESEL	Total petroleum hydrocarbons - diesel range	4	ECF-100NR2-0053	
TPHGASOLIN E	Total petroleum hydrocarbons - gasoline range	4	ECF-100NR2-0053	
TPH/OILH	Total petroleum hydrocarbons - motor oil (high boiling)	4	ECF-100NR2-0053	
88-85-7	Dinoseb(2-secButyl-4,6-dinitrophenol)	4.3	EPA, 2012	
7439-95-4	Magnesium	4.5	EPA, 2012	
83-32-9	Acenaphthene	4.9	CLARC, 2014	
208-96-8	Acenaphthylene	5.0	ORNL, 2014	
7782-49-2	Selenium	5.0	CLARC, 2014	
7440-09-7	Potassium	5.5	EPA, 2012	
7440-43-9	Cadmium	6.7	CLARC, 2014	
86-73-7	Fluorene	7.7	CLARC, 2014	
7440-22-4	Silver	8.3	CLARC, 2014	
11141-16-5	Aroclor-1232	8.4	EPA, 2012	
11104-28-2	Aroclor-1221	8.4	EPA, 2012	
132-64-9	Dibenzofuran	9.2	EPA, 2012	
76-44-8	Heptachlor	9.5	CLARC, 2014	
53494-70-5	Endrin ketone	9.7	ORNL, 2014	
57-12-5	Cyanide	9.9	EPA, 2012 <sup>b</sup>	
1031-07-8	Endosulfan sulfate	9.9	ORNL, 2014	

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (K<sub>d</sub>) in Ascending Mobility Order

CAS#	Constituent Name	Selected K <sub>d</sub> (mL/g)	Source of Selected K <sub>d</sub>
72-20-8	Endrin	11	CLARC, 2014
85-68-7	Butylbenzylphthalate	14	CLARC, 2014
85-01-8	Phenanthrene	17	ORNL, 2014
7439-98-7	Molybdenum	20	EPA, 2012 b
7440-50-8	Copper	22	CLARC, 2014
120-12-7	Anthracene	23	CLARC, 2014
7439-89-6	Iron	25	EPA, 2012 b
60-57-1	Dieldrin	26	CLARC, 2014
7440-38-2	Arsenic	29	CLARC, 2014
7440-24-6	Strontium	35	EPA, 2012 b
7440-39-3	Barium	41	CLARC, 2014
7440-36-0	Antimony	45	CLARC, 2014
7440-48-4	cobalt	45	EPA, 2012 b
72-54-8	4,4'-DDD (Dichlorodiphenyldichloroethane)	46	CLARC, 2014
309-00-2	Aldrin	49	CLARC, 2014
206-44-0	Fluoranthene	49	CLARC, 2014
5103-71-9	Alpha-Chlordane	51	CLARC, 2014
57-74-9	Chlordane	51	CLARC, 2014
7439-97-6	Mercury	52	CLARC, 2014
87-68-3	Hexachlorobutadiene	54	CLARC, 2014
7440-66-6	Zinc	62	CLARC, 2014
7439-96-5	Manganese	65	EPA, 2012 b
7440-02-0	Nickel	65	CLARC, 2014
129-00-0	Pyrene	68	CLARC, 2014
7440-28-0	Thallium	71	CLARC, 2014
12672-29-6	Aroclor-1248	77	EPA, 2012
53469-21-9	Aroclor-1242	78	EPA, 2012
118-74-1	Hexachlorobenzene	80	CLARC, 2014
72-43-5	Methoxychlor	80	CLARC, 2014
1024-57-3	Heptachlor epoxide	83	CLARC, 2014
72-55-9	4,4'-DDE (Dichlorodiphenyldichloroethylene)	86	CLARC, 2014
8001-35-2	Toxaphene	96	CLARC, 2014

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (K<sub>d</sub>) in Ascending Mobility Order

CAS#	Constituent Name	Selected K <sub>d</sub> (mL/g)	Source of Selected K <sub>d</sub>	
7440-23-5	Sodium	100	EPA, 2012 <sup>b</sup>	
12674-11-2	Aroclor-1016	107	CLARC, 2014	
117-81-7	Bis(2-ethylhexyl) phthalate	111	CLARC, 2014	
11097-69-1	Aroclor-1254	131	EPA, 2012	
16984-48-8	Fluoride	150	EPA, 2012 b	
77-47-4	Hexachlorocyclopentadiene	200	CLARC, 2014	
7440-31-5	Tin	250	EPA, 2012 b	
7439-93-2	Lithium	300	EPA, 2012 b	
56-55-3	Benzo(a)anthracene	358	CLARC, 2014	
218-01-9	chrysene	398	CLARC, 2014	
50-29-3	4,4'-DDT (Dichlorodiphenyltrichloroethane)	678	CLARC, 2014	
7440-41-7	Beryllium	790	CLARC, 2014	
11096-82-5	Aroclor-1260	822	CLARC, 2014	
50-32-8	Benzo(a)pyrene	969	CLARC, 2014	
7440-47-3	Chromium	1,000	CLARC, 2014	
7440-62-2	Vanadium	1,000	CLARC, 2014	
205-99-2	Benzo(b)fluoranthene	1,230	CLARC, 2014	
207-08-9	Benzo(k)fluoranthene	1,230	CLARC, 2014	
7429-90-5	Aluminum	1,500	EPA, 2012 <sup>b</sup>	
53-70-3	Dibenz[a,h]anthracene	1,789	CLARC, 2014	
191-24-2	Benzo(ghi)perylene	1,950	ORNL, 2014	
193-39-5	Indeno(1,2,3-cd)pyrene	3,470	CLARC, 2014	
7439-92-1	Lead	10,000	CLARC, 2014	
117-84-0	Di-n-octylphthalate	83,200	CLARC, 2014	
7440-69-9	Bismuth			
24959-67-9	Bromide		EPA, 2012	
7440-70-2	Calcium		EPA, 2012	
14265-44-2	Phosphate		EPA, 2012	
7440-21-3	Silicon		EPA, 2012	
65794-96-9	3+4 Methylphenol (cresol, m+p)			
PCB1242/1016	Co-elution of Aroclor 1242 and Aroclor 1016		EPA, 2012	
7440-61-1	Uranium	NVR°	-	

Table 5-5. Summary of Nonradiological Analyte Distribution Coefficients (Kd) in Ascending Mobility Order

		Selected K <sub>d</sub>	
CAS#	Constituent Name	(mL/g)	Source of Selected K <sub>d</sub> <sup>a</sup>

- a. Sources of Selected K<sub>d</sub> values:
  - Ecology, 2014, "Cleanup Levels and Risk Calculations (CLARC)" database, Washington State Department of Ecology, available at: <a href="https://fortress.wa.gov/ecy/clarc/">https://fortress.wa.gov/ecy/clarc/</a>.
  - EPA, 2012, "Regional Screening Levels for Chemical Contaminants at Superfund Sites," U.S. Environmental Protection Agency, updated November 2012, available at: <a href="http://www.epa.gov/reg3hscd/risk/human/rb-concentration\_table/">http://www.epa.gov/reg3hscd/risk/human/rb-concentration\_table/</a>.
  - ECF-100NR2-0053, Saturated Zone Flow and Transport Modeling in Support of 100-N RI/FS Document.
  - ECF-Hanford-11-0165, Evaluation of Hexavalent Chromium Leach Test Data Conducted on Vadose Zone Sediment Samples from the 100 Area, in Appendix F.
  - ORNL, 2014, "Risk Assessment Information System," Oak Ridge National Laboratory, available at: http://rais.ornl.gov/.
- b. Source: EPA, 2012, Section 4.12, "Soil to Groundwater."
- c. NVR [No Value Required]. Uranium is not modeled because uranium is not a soil COPC at 183-H or other 100-D/H locations. Uranium will be monitored as a GW COPC.

CAS = Chemical Abstracts Service

COPC = contaminants of potential concern

EPA = U.S. Environmental Protection Agency

GW = groundwater

Table 5-6. Summary of Radiological Analyte Distribution Coefficients (K<sub>d</sub>) in Ascending Mobility Order

CAS#	Radionuclide	$K_{d} \ (mL/g)$	Source
14133-76-7	Technetium-99	0	DOE/RL-96-17
10028-17-8	Tritium	0	DOE/RL-96-17
15046-84-1	Iodine-129	1	DOE/RL-96-17
13966-00-2	Potassium-40	5.5	DOE/RL-96-17
13966-32-0	Sodium-22	. 10	DOE/RL-96-17
13994-20-2	Neptunium-237	15	DOE/RL-96-17
10098-97-2	Strontium-90	25	DOE/RL-96-17
13981-37-8	Nickel-63	30	DOE/RL-96-17
10045-97-3	Cesium-137	50	DOE/RL-96-17
10198-40-0	Cobalt-60	50	DOE/RL-96-17
14391-65-2m	Silver-108m	90	DOE/RL-96-17
14596-10-2	Americium-241	200	DOE/RL-96-17
14762-75-5	Carbon-14	200	DOE/RL-96-17
15757-87-6	Curium-243	200	DOE/RL-96-17
13981-15-2	Curium-244	200	DOE/RL-96-17
14683-23-9	Europium-152	200	DOE/RL-96-17

Table 5-6. Summary of Radiological Analyte Distribution Coefficients (Kd) in Ascending Mobility Order

CAS#	Radionuclide	$K_d$ (mL/g)	Source
15585-10-1	Europium-154	200	DOE/RL-96-17
14391-16-3	Europium-155	200	DOE/RL-96-17
14681-63-1	Niobium-94	200	DOE/RL-96-17
13981-16-3	Plutonium-238	200	DOE/RL-96-17
15117-48-3	Plutonium-239	200	DOE/RL-96-17
PU-239/240	Plutonium-239/240	200	DOE/RL-96-17
14119-33-6	Plutonium-240	200	DOE/RL-96-17
14119-32-5	Plutonium-241	200	DOE/RL-96-17
13982-63-3	Radium-226	200	DOE/RL-96-17
15262-20-1	Radium-228	200	DOE/RL-96-17
14274-82-9	Thorium-228	200	DOE/RL-96-17
14269-63-7	Thorium-230	200	DOE/RL-96-17
7440-29-1	Thorium-232	200	DOE/RL-96-17

Source of selected K<sub>d</sub> values: DOE/RL-96-17, Remedial Design Report/Remedial Action Work Plan for the 100 Area.

STOMP simulations were run for 1,000 years to produce peak groundwater concentrations for all the  $K_d$  values required for all COPCs.

#### 5.4.4 Matric Potential

The matric potential is a measure of the attractive forces between water and porous or fractured materials that are important during variably saturated flow conditions in the vadose zone (*Vadose Zone Processes* [Selker et al., 1999]). Moisture content and hydraulic conductivity are functions of matric potential. These functions are typically nonlinear and must be determined for each rock or soil type. The combination of matric potential gradients and gravity constitute the most important driving forces for vadose zone flow. The soil covers discussed in the preceding section will cause variations in the moisture and matric potential, in accordance with the net infiltration allowed by each cover.

Like pressure head, matric potential can be measured in the field and in the laboratory. In situ measurements of matric potential in the shallow Hanford Site vadose zone have been made using tensiometers and heat-dissipation sensors in lysimeters, pits, and boreholes (Compendium of Data for the Hanford Site (Fiscal Years 2004 to 2008) Applicable to Estimation of Recharge Rates [PNNL-17841]; Hydrologic Characterizations Using Vadose Zone Monitoring Tools: Status Report [PNNL-14115]; and Soil Water Balance and Recharge Monitoring at the Hanford Site – FY09 Status Report [PNNL-18807]).

The nonlinear relationship between water content and matric potential, frequently called the moisture retention or characteristic curve, can usually be measured in the laboratory. The much greater nonlinearity of the hydraulic conductivity and matric potential constitutive relation, termed the relative permeability, can typically be measured only over a small range of matric potential values. The remainder of the matric

potential range must be inferred, because the hydraulic conductivity can decrease several orders of magnitude for a much smaller decrease in matric potential.

The "A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils" (van Genuchten, 1980) alpha and *n* parameters used in the STOMP 1D simulations were selected to represent materials from 100-D/H and help define the relationship between moisture content in variably saturated media, the matric potential, and relative permeability. The inputs used in the simulations are described in detail in *STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units* (ECF-HANFORD-11-0063) in Appendix F.

#### 5.5 Batch Leach Tests

Batch leach tests were conducted on soil samples from selected boreholes, wells, and test pits during the 100-D/H RI to establish estimated  $K_d$  values to support modeling needs, as described in the 100-D/H SAP (DOE/RL-2009-40). Contamination present in pore water within the bulk soil matrix was not analyzed, or accounted for separately, because the associated contaminant mass is included within the bulk leachate concentrations. The  $K_d$  calculations for each contaminant and each dilution ratio were performed using the analytical results from bulk soil analysis and leach testing of material collected from the same location.

#### 5.5.1 Batch Leach Test Methodology

Batch leach tests were performed on soil and aquifer sediment samples using a leach procedure based on Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM D3987-06). The procedure was performed using a 2 mm sieve to include the entire sand fraction based on the U.S. Department of Agriculture scheme for soil grain-size classification. Where insufficient sample mass with less than 2 mm particle diameter was available based on actual field conditions, a 3/8 in. mesh screen was used instead. Demineralized water, pH-adjusted according to EPA's West Coast recommendation, was used as the leaching liquid. Selected soil samples were leached at soil to water weight ratios of 1 to 1, 1 to 2.5, and I to 5, with one test in each series duplicated. Soil/water mixtures were placed in clean, water-tight sample containers (extraction vessels) and rotated end over end through the vessel centerline at a rate of about 30 rotations per minute for 18 hours. Following 18 hours of mixing, the soil/water slurry was filtered using a 0.45 µm filter. The leachate was analyzed for pH and conductivity. The leachate, after the 18-hour extraction period, and untreated soil were analyzed for arsenic, barium, cadmium, total chromium and Cr(VI), lead, selenium, and silver. Metals analysis for leachate and soil digests was performed using EPA Methods 6010, 6020, or 200.8 for ICP metals, as applicable (bulk soil was digested using EPA Method 3050B or 3051 for metals and EPA Method 3060A for Cr(VI) to prepare for analysis). Separate aliquots of material were used for bulk soil analysis and leaching.

The  $K_d$  is calculated as the ratio of the contaminant sorbed to material to the contaminant in solution by the following equation:

$$K_d = \frac{(C_S \times M_S)(C_L \times V_L)}{M_S} \times \frac{1000}{C_L}$$

where:

 $K_d$  = soil-water distribution coefficient (mL/g)

 $C_S$  = contaminant concentration in bulk soil matrix before leaching ( $\mu g/g$ )

 $M_S$  = dry mass of soil used for leaching (g)

 $C_L$  = contaminant concentration in leachate ( $\mu$ g/L)

 $V_L$  = liquid volume used for leaching (L)

For each vadose zone soil sample, four replicate samples were analyzed for total soil metal concentrations. The average of the four measurements was used in the calculation of  $K_d$ . If one or more of the four replicates was found to be below reporting limit, the sample concentration was not considered reliable enough to report a  $K_d$  value. This was done because the reporting limit varied among replicates, with the reporting limit for one replicate often being several times that of another. This variation precluded the use of surrogate values such as half-reporting limits because of the significant uncertainty introduced by the variable reporting limits. In most cases, more than one or all four replicates were below reporting limit. For duplicate samples, the larger  $K_d$  of the two was reported. Often, an average soil concentration was calculated but the leachate water concentration was below reporting limit: in this event, the reporting limit was substituted in the calculation of a minimum  $K_d$  value, and a greater than (>) sign was placed before the calculated  $K_d$  value in the table.

The batch leaching of soil samples collected from 100-D/H was conducted on many uncontaminated soil samples collected during the RI characterization process. As a result, most of the 251 samples selected for batch leach testing were found to contain either no detectable residues of the analytes of interest in the bulk sample or no detectable analyte of interest in the extract; in those situations, the estimate of  $K_d$  is not quantifiable. The only analyte consistently detected in bulk samples and in the batch leaching extract was barium. Cr(VI) was detected in a few batch leaching extract samples. Cr (total) was detected in 77 sample intervals of 251 samples collected from 29 locations while Cr(VI) was detected in only 9 of 251 batch leach extracts from the same 29 locations. From this, it can be inferred for Cr(VI) that a significant fraction of chromium is non-leachable and that much of the chromium may be in Cr(III) form. There are, however, anomalies that are a key component of the CSM (Section 4.9) that may provide an explanation for the north plume that currently does not have an identified source. The details of the batch leach testing results are presented separately in 100-D and 100-H Remedial Investigation Distribution Coefficient Calculations (0100X-CA-V0059), in Appendix F.

## 5.5.2 Development of a Hexavalent Chromium Distribution Coefficient for Vadose Simulations from Batch Leach Testing Results

The results of the batch leach testing for Cr(VI) were further evaluated to identify a single derived  $K_d$  value to represent Cr(VI) behavior in the vadose zone model, which were then used to calculate peak groundwater concentrations used to derive SSLs and PRGs.

The results of leach tests described in 100-D and 100-H Remedial Investigation Distribution Coefficient Calculations (0100X-CA-V0059) were analyzed (along with data from other river corridor OUs (100-B/C, 100-K, 100-F/IU [ECF-HANFORD-11-0165; Appendix F]) to estimate an area-wide K<sub>d</sub> value for residual Cr(VI) in the vadose zone including D/H area samples. ECF-HANFORD-11-0063, Section 3.4 in Appendix F provides additional information on sample locations. The assessment of K<sub>d</sub> relies on collected field data and the corresponding laboratory analysis outlined in the 100-D/H SAP (DOE/RL-2009-40) to recommend a K<sub>d</sub> value for use in the 100 Area. All methods used to calculate a value for K<sub>d</sub> were outlined in the 100-D/H SAP (DOE/RL-2009-40) for each respective OU along the River Corridor. The objective of this evaluation is to recommend a K<sub>d</sub> for use in the River Corridor, including 100-D/H. Details of the analysis are described in Evaluation of Hexavalent Chromium Leach Test Data Conducted on Vadose Zone Sediment Samples from the 100 Area (ECF-HANFORD-11-0165) in Appendix F. The batch leach testing evaluation of data collected in 100-D/H is presented in Appendix C. A total of 31 boreholes and wells were included in the batch leach testing, and most had very low leachate levels (<100 μg/L) with two exceptions, at boreholes C7862 and C7866 that had higher

leachate concentrations. These results, along with results from other River Corridor OUs, were used in Evaluation of Hexavalent Chromium Leach Test Data Conducted on Vadose Zone Sediment Samples from the 100 Area (ECF-HANFORD-11-0165) in Appendix F.

To establish a representative  $K_d$  value for use in the River Corridor, the calculated  $K_d$  values were adjusted for the amount of water used during the tests normalizing the values to the smallest soil; water extract ratio. This resulted in a 90<sup>th</sup> percentile exceedance  $K_d$  value of 0.8 mL/g (here, a 90<sup>th</sup> percentile exceedance means there is a 0.9 probability that the  $K_d$  value will be greater than or equal to 0.8 mL/g). Based on the batch leach results for soil samples collected from all of the 100 Area, a  $K_d$  value of 0.8 mL/g was designated as a conservative estimate for the lower limit on residual Cr(VI)  $K_d$  value for the River Corridor.

The results of batch leach testing using the method specified in the SAP are subject to some degree of uncertainty because of the test method and the computational approach to calculating resulting  $K_d$ . Specific areas of uncertainty identified to apply to the derivation of contaminant-specific  $K_d$ s are described in *Evaluation of Hexavalent Chromium Leach Test Data Conducted on Vadose Zone Sediment Samples from the 100 Area* (ECF-HANFORD-11-0165) (Appendix F). The following general topics may produce some uncertainty in derivation of  $K_d$  values from batch leach testing measurements:

- Differences in the pH of the extract solutions used to prepare the solid phase and liquid phase for analysis
- Dilution effects of batch leaching at differing solid to liquid ratios
- Variations in the linearity of the measured K<sub>d</sub> values
- Effects of the coarse material (that is, gravel fraction) on the effective K<sub>d</sub> of the formation
- Potential dilution effects of adding potable water to boreholes during drilling

The site-specific value selected for Cr(VI) is considered bounding because it was selected on the basis that 90 percent of the  $K_d$  values in that analysis had higher sorption values. Thus, this value would not be appropriate to represent hexavalent chromium migration in a predictive model, but is appropriate for use in this bounding calculation of SSL and PRG values. Further, this value for  $K_d$  of hexavalent chromium is applicable only to the residual fraction of hexavalent chromium remaining in the vadose zone; it is inapplicable to the mobile fraction that migrated out of the vadose zone in the past.

## 5.6 Vadose Zone Modeling Methods and Results

The methodology described here constitutes the use of an alternative fate and transport model as defined in WAC 173-340-747, "Deriving Soil Concentrations for Groundwater Protection." A crosswalk is provided in Attachment A of ECF-HANFORD-11-063 (Appendix F) that demonstrates how this methodology meets the pertinent requirements of WAC 173-340-747.

Vadose zone transport simulations for this activity were performed using the STOMP code with a series of input values for sensitive variables based to the extent possible on conditions observed or measured at representative locations at 100-D and 100-H. The model development for vadose zone models used to support this RI is comprehensively documented in *Model Package Report: Vadose Zone Model for the River Corridor* (SGW-50776). The numerical approach for calculations made using this model is described in detail in *STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units* (ECF-HANFORD-11-0063) in Appendix F, but a brief summary is presented here. One-dimensional

numerical models were constructed to represent the key facets of the conceptual model and were solved using the STOMP code (STOMP: Subsurface Transport Over Multiple Phases Version 2.0: Theory Guide [PNNL-12030]). The STOMP-W (water) mode was used to solve the Richards equation (termed the water mass conservation equation in STOMP) and the advection-dispersion equation (termed the solute mass conservation equation in STOMP) that govern unsaturated water flow and dilute solute transport, respectively, under variably saturated conditions in porous media. The STOMP numerical simulations were performed to obtain the magnitude and time of peak groundwater concentrations for COPCs for the various recharge rates, sediment types and thicknesses, and hydraulic properties applicable to 100-D/H. Numerical transport simulations were run to simulate 1,000 years from the present (based on regulator comment). Thus, only a subset of the 100 Area COPCs that were likely to have peak groundwater concentrations occur within that period were simulated. Simulated peak groundwater concentrations were then used to compute SSLs and PRGs.

Conceptually, the model represents a column of sediments that comprise a vadose zone underlain by an aquifer. Recharge-driven flow moves downward through the vadose zone, where it encounters contamination that is eventually transported to an underlying aquifer, across which a pressure gradient drives horizontal flow. At the start of each vadose transport simulation, the vadose zone is composed of a cover of clean fill with constant thickness as well as contaminated and uncontaminated sediments of varying thickness. The aquifer constitutes the base of the column with a minimum thickness of 5 m (16 ft), so that a 5 m (16 ft) long monitoring well screen could be simulated. Within the 100-D/H source OU, the vadose zone is composed of either the Hanford formation alone or a combination of the Hanford formation and Ringold Formation unit E. In contrast, the saturated zone can comprised of only the Hanford formation or only the Ringold Formation unit E. Underlying 100-D, the Ringold Formation unit E/RUM contact forms the base of the unconfined aquifer. Underlying most of the Horn area and 100-H, the Hanford formation/RUM contact forms the base of the unconfined aquifer. The derived K<sub>d</sub> for Cr(VI) of 0.8 mL/g was applied to Cr(VI) in all vadose zone strata in the model. This K<sub>d</sub> value used for Cr(VI) is applicable only to the residual remaining in the vadose zone, and not the leachable fraction that has previously migrated to groundwater.

The STOMP code input parameters are summarized in Table 5-7 for the screening level and PRG calculations for 100-D/H.

Table 5-7. Summary of Selected Primary Fate and Transport Simulation Input Parameters
Used with 1-D Model Implemented in the STOMP Code for Screening Level and
Preliminary Remediation Goal Calculations in 100-D and 100-H Operable Units<sup>a</sup>

Input Parameter (units)	Input Parameter Value					
Simulation Duration						
Simulation to establish initial hydraulic conditions (yr)	Calendar years 0 to 2010 (arbitrary long period to reach a steady state)					
Simulation to predict contaminant transport (yr)	Calendar years 2010 to 3010					
Upper Boundary Condition: Rec	charge (Deep Percolation) for Different Surface Soils (stepwise constant)					
Native Vegetation Recharge Scenario	Hanford sand, disturbed					
Recharge before 1880 (mm/yr) "Pre-Settlement"	4.0					
Recharge 1880 to 1944 (mm/yr) "Historic Irrigation"	72.4					

Table 5-7. Summary of Selected Primary Fate and Transport Simulation Input Parameters Used with 1-D Model Implemented in the STOMP Code for Screening Level and Preliminary Remediation Goal Calculations in 100-D and 100-H Operable Units<sup>a</sup>

Input Parameter (units	s)			Input Paramete	r Value	
Recharge 1944 to 2010 (mm/y "Hanford Operations"	/r)	63.0				
Recharge 2010 to 2015 (mm/y "Bare Soil"	/r)	63.0				
Recharge 2015 to 2020 (mm/y "Cheatgrass"	r)					
Recharge 2020 to 2050 (mm/y "Developing Shrub-Steppe"	/r)	8.0				
Recharge after 2050 (mm/yr) "Mature Shrub-Steppe"		4.0				
Irrigation Recharge Scena	ario			Hanford sand, d	isturbed	
Recharge before 1880 (mm/yr "Pre-Settlement"	)			4.0		
Recharge 1880 to 1944 (mm/y "Historic Irrigation"	r)	72.4				
Recharge 1944 to 2010 (mm/y "Hanford Operations"	r)	63.0				
Recharge 2010 to 2015 (mm/y "Bare Soil"	т)	63.0				
Recharge 2015 to 2045 (mm/y "Irrigation I"	T)	76.4				
Recharge after 2045 (mm/yr) "Irrigation II"				72.4		
Lateral B	oundar	y Cond	lition: Hydraulic	Gradient (Satura	ited Portion)	
100-D hydraulic gradient (m/n	n)		_	0.0011		
100-H hydraulic gradient (m/n	n)			0.0021		
			Hydraulic Paran	neters		
			Vados	e Zone	Saturat	ed Zone
100-D Operable Units <sup>b</sup>	Back	kfill	Hanford formation	Ringold Formation	Hanford formation	Ringold Formation
$n_T$ total porosity (m <sup>3</sup> /m <sup>3</sup> )	0.2	76	0.280	0.293	0.280	0.293
$n_D$ diffusive porosity $(m^3/m^3)$	0.2					0.267
α van Genuchten water retention function inverse air entry matric potential (1/cm)	0.0	0.029 0.013 0.029			0.013	
n van Genuchten water retention function exponential fitting parameter (dimensionless)	1.4	00	1.378	1.538	1.378	1.538

Table 5-7. Summary of Selected Primary Fate and Transport Simulation Input Parameters Used with 1-D Model Implemented in the STOMP Code for Screening Level and Preliminary Remediation Goal Calculations in 100-D and 100-H Operable Units<sup>a</sup>

Input Parameter (units	)		Input Parameter	Value	
s <sub>r</sub> residual saturation (dimensionless)	0.103	0.022	0.057	0.022	0.057
<i>K<sub>s,h</sub></i> saturated horizontal hydraulic conductivity (m/d)	0.517	4.03	0.819	55.5	22.4
K <sub>s,ν</sub> saturated vertical hydraulic conductivity (m/d)	0.517	0.403	0.0819	5.55	2.24
		Vado	se Zone	Saturat	ed Zone
100-H Operable Units <sup>b</sup>	Backfill	Hanford formation	Ringold Formation	Hanford formation	Ringold Formation
$n_T$ total porosity (m <sup>3</sup> /m <sup>3</sup> )	0.276	0.280	0.293	0.280	0.293
$n_D$ diffusive porosity $(m^3/m^3)$	0.262	0.247	0.267	0.247	0.267
α van Genuchten water retention function inverse air entry matric potential (1/cm)	0.019	0.029	0.013	0.029	0.013
n van Genuchten water retention function exponential fitting parameter (dimensionless)	1.400	1.378	1.538	1.378	1.538
s <sub>r</sub> residual saturation (dimensionless)	0.103	0.022	0.057	0.022	0.057
K <sub>s,h</sub> saturated horizontal hydraulic conductivity (m/d)	0.517	4.03	0.819	97.6	3.70
K <sub>s,ν</sub> saturated vertical hydraulic conductivity (m/d)	0.517	0.403	0.0819	9.76	0.370
Both 100-D and 100-H Operable Units <sup>b</sup>	Backf	fill .	Hanford formation	Ringol	d Formation
$\rho_p$ particle density (g/cm <sup>3</sup> )	Calculated from bulk density and porosity; $\rho_p = \rho_b / (1 - n_T)$				
$\rho_b$ bulk density (g/cm <sup>3</sup> )	1.94 1.93 1.93		1.93		
m Mualem relative permeability function fitting parameter (dimensionless)			m=(n-1)/n		
β Mualem relative permeability function exponential term			0.5		
		Transport Para	meters		
$D_m$ molecular diffusion (m <sup>2</sup> /s)	Conventional n	model with $D_m =$	0		
$\alpha_L$ longitudinal dispersivity (m)	0 (dispersivity ne	eglected; conserv	ative assumption wi	th regard to peal	k concentration)
$\alpha_{T}/\alpha_L$ dispersivity anisotropy ratio (dimensionless)	Not applicable	(one-dimensiona	il model)		

Table 5-7. Summary of Selected Primary Fate and Transport Simulation Input Parameters
Used with 1-D Model Implemented in the STOMP Code for Screening Level and
Preliminary Remediation Goal Calculations in 100-D and 100-H Operable Units<sup>a</sup>

Input Parameter (units	s)	Input Parameter Value
$K_d$ distribution coefficient (mL/g)	using t ECF-H	PPCs (187 nonradionuclides and 25 radionuclides) were simulated directly he specific contaminant $K_d$ values for each contaminant evaluated as listed in IANFORD-10-0063 (found in Appendix F) in Attachment B, Tables B-1, -3, B-4, B-5, and B-6; and in Attachment C, Tables C-1, C-2, C-3, C-4, C-5, 6.

Sources: Mualem, 1976, "A New Model for Predicting the Hydraulic Conductivity of Unsaturated Porous Media." van Genuchten, M.Th, 1980, "A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils."

COPC = contaminant of potential concern

#### 5.6.1 Representation of Initial Contaminant Distribution

The calculation of SSL and PRG values is completed in a two-step process. In the first forward calculation step, STOMP is used to calculate the peak groundwater concentration that results from an initial unit source concentration (1.0 mg/kg for nonradionuclide COPCs, or 1.0pCi/kg for radionuclide COPCs, soil concentration) that is uniformly applied over the assumed contaminated thickness of the vadose zone. The resulting peak groundwater concentration is then be used in a second, back-calculation step to determine SSL and PRG values. The second, or back-calculation, step involves scaling the peak groundwater concentration against the appropriate regulatory compliance criteria to back-calculate the maximum initial soil concentration that would not result in an exceedance. The maximum value obtained from this back-calculation step is assigned as the SSL or PRG value (depending on the recharge scenario used). As a measure of maximum allowable contaminant concentration in the soil, SSLs and PRGs are expressed as contaminant mass per mass of soil for non-radionuclides (e.g., mg/kg) and as contaminant activity per mass of soil for radionuclides (e.g., pCi/kg). The use of a unit initial concentration in STOMP in the forward-calculation step is strictly a convenience to support calculation of SSLs and PRGs in a back-calculation step. The unit concentration therefore is not to be confused as constituting an actual observed waste site residual soil concentration. Further detail on this approach is provided in Appendix F (ECF-Hanford-11-0063 and Model Package Report: Vadose Zone Model for the River Corridor [SGW-50776]).

The initial simulation configuration was developed assuming that interim remedial actions have been undertaken and that 4.6 m (15 ft) of clean backfill is present starting at the ground surface. Note that this assumption is approximately representative of conditions at any particular waste site, where interim action excavations may have proceeded to greater or lesser depth.

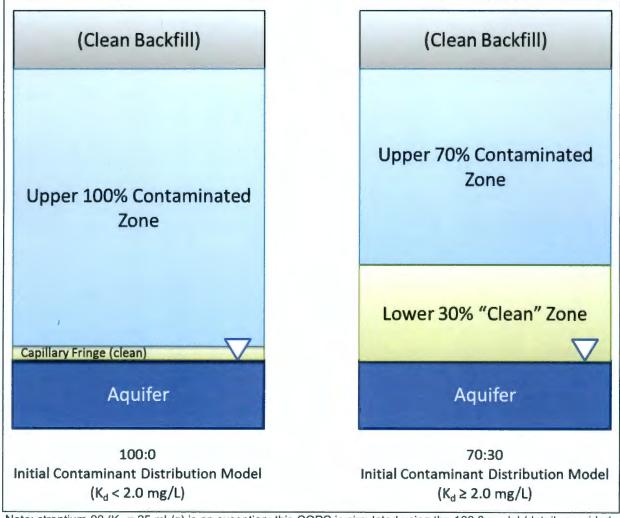
Contaminant spatial distributions were identified for use in initial flow and transport simulations based on observations of contaminant distribution made from RI soil sample analysis. Numerous contaminants were found to be distributed throughout the thickness of the vadose zone; others exhibited limited vertical distribution. For the source distribution, all the contaminants were grouped into two categories, one with low  $K_d$  ( $\leq 2 \text{ mL/g}$ ) and another with high  $K_d$  ( $\geq 2 \text{ mL/g}$ ). The process of identification of low  $K_d$  range

a. Details on the basis for all parameters in this table are found in Appendix F (STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units [ECF-HANFORD-11-0063]).

b. Values for these model input parameters are assigned based on whether the site is located in the 100-D or 100-H Area Operable Units.

and high K<sub>d</sub> range is presented in Conceptual Basis for Distribution of Highly Sorbed Contaminants in 100 Areas Vadose Zone (SGW-51818; Appendix F).

For low  $K_d$  (< 2 mL/g) contaminants (and strontium-90; see discussion below), a uniform unit concentration of was applied to the entire vadose zone from below the clean backfill to a depth 0.5 m (1.6 ft) above the water table (representing the capillary fringe) for the forward calculation using STOMP; this is referred to as the 100:0 profile. This 100:0 profile represents contamination as present throughout the soil column at a peak concentration, excluding backfill and the capillary fringe (Figure 5-5). Initial concentration in the 0.5 m (1.6 ft) zone above the water table was not applied due to physical presence of capillary fringe and water table movement in the periodically rewetted zone that would result from river stage fluctuations. Placing the initial mass at the water table at the start of the simulation would result in boundary effects and extreme-concentration gradients.



Note: strontium-90 (K<sub>d</sub> = 25 mL/g) is an exception; this COPC is simulated using the 100:0 model (details provided in text).

Figure 5-5. Depiction of 100:0 and 70:30 Initial Contaminant Distribution Models

For the higher  $K_d$  ( $\geq 2$  mL/g) contaminants, a uniform unit concentration was applied in the upper 70 percent of the vadose zone below the clean backfill for the forward calculation using STOMP; this is referred to as the 70:30 profile. This 70:30 profile assumes contamination represents contamination as present in the top 70 percent of the soil column excluding backfill (Figure 5-5).

An exception to the assignment of initial source distributions based on  $K_d$  is made in the case of strontium-90, owing to the observed distribution of this COPC at depths greater than the upper 70 percent of the profile for this COPC in numerous locations. This distribution is a legacy of the greater mobility of this contaminant in the operational era under different geochemical and hydraulic conditions than are prevalent in the present or anticipated in the future. Accordingly, despite a  $K_d$  value higher than the 2 mL/g threshold, the 100:0 profile is applied for evaluation of strontium-90.

The 100:0 and 70:30 profiles can be considered to be bounding for the following reason. SSL and PRG are derived from a back-calculation from STOMP simulations of a profile that is uniformly contaminated over the appropriate vadose zone range (100:0 or 70:30 profile). Therefore, the SSL or PRG value represents the entire contaminated range as contaminated at the level compared to the EPC value. In actual soil profiles, finding contamination uniformly distributed over such a range at this level is highly unlikely. In this respect, the 100:0 is clearly bounding, because a greater contamination range cannot be applied. The 70:30 profile is bounding, provided the conceptual model provided in *Conceptual Basis for Distribution of Highly Sorbed Contaminants in 100 Areas Vadose Zone* (SGW-51818) is representative. Note that in the case of strontium-90, it was not, and hence the 100:0 profile was applied for that COPC. Questions as to the bounding response of the 70:30 profile also were evaluated with regard to observed vertical distributions in RI boreholes (discussed in Section 5.7.2).

Although the same contaminant distribution was applied to calculate both the SSLs and the PRGs, a different infiltration/recharge scenario was applied to each simulation. The SSL simulation uses a maximum foreseeable recharge scenario based on irrigated agriculture land use. The PRG simulation, alternatively, uses a recharge scenario based on the expected future land use: conservation, with a native plant population re-established at the land surface. Recharge scenarios are presented in Section 5.4.1. SSL and PRG values are compared to EPCs in Section 5.7.3.

Additional details on the initial contaminant distribution is provided in the model package report (*Model Package Report: Vadose Zone Model for the River Corridor* [SGW-50776]; Appendix F) documenting the model development and to the environmental calculation file (ECF-HANFORD-11-0063; Appendix F) documenting the model application to 100-D/H.

#### 5.6.2 Simulation Duration

The simulation time for calculating screening values and PRGs was limited to 1,000 years based on regulator comment. The peak groundwater concentration within the 1,000-year simulation was used to determine the SSL and PRG values.

# 5.7 Groundwater/Surface Water Protection Screening Level and Preliminary Remediation Goal Development

The SSLs and PRGs were developed to provide an basis to identify waste site contaminants that may pose a threat for continuing contribution to groundwater and surface water contamination (STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units [ECF-HANFORD-11-0063] in Appendix F). The SSLs and PRGs are based on an assumption of uniform vadose zone contamination over a bounding portion of the soil column (100:0 initial source profile for lower K<sub>d</sub> contaminants plus strontium-90; 70:30 profile for higher K<sub>d</sub> contaminants except strontium-90). The initial condition (either the 100:0 or 70:30 model) represents a bounding initial condition in terms of soil concentration that effectively assumes the maximum residual soil contamination level is uniformly present over the entire applicable vadose zone thickness (considered bounding because this peak concentration would highly unlikely to persist over the full range) appropriate to the K<sub>d</sub> range (Conceptual Basis for Distribution of Highly Sorbed Contaminants

in 100 Areas Vadose Zone [SGW-51818]). SSLs were calculated assuming a recharge scenario based on the maximum foreseeable recharge scenario, irrigated agriculture. In contrast, PRGs were calculated assuming a recharge scenario based on the expected land use, conservation. Comparison of site EPCs to SSLs provided a screening level to identify those constituents that likely pose a continuing threat under the bounding condition of irrigated agriculture land use. Those sites that failed this screening were then compared to PRGs based on expected land use to identify those constituents that likely pose a continuing threat under conservation land use.

SSLs and PRGs represent the maximum concentration, whether mass concentration (for nonradionuclides) or activity concentration (for radionuclides) in soil, of specific contaminants that can remain in the vadose zone after remedial action without causing an exceedance of a potential ARAR (Chapter 8) or risk-based value for protection of groundwater or surface water. The value of a SSL or PRG for a particular COPC depends on a small number of key factors:

- COPC initial vertical distribution (the portion of the vadose zone that is contaminated, and the
  distance of that contamination relative to the water table below) and horizontal extent of
  contamination represented by the waste site dimension in the direction of groundwater flow (the
  approach allows for scaling the SSL or PRG value to this dimension).
- Recharge rate, which is a function of land cover (surface soil type and vegetation cover); for future
  conditions, this in turn is a function of the expected land use (irrigated agriculture or conservation
  with native vegetation)
- Interactions between vadose zone geology and water movement (hydraulic parameters)
- COPC characteristics (sorption and decay, where applicable)

Some of these key factors are represented in a conservative approach to ensure the PRGs are not overestimated. For example, the COPC initial distributions are intentionally bounding relative to observed COPC vertical distributions in the vadose zone (Chapter 4). This is bounding because the approach effectively assumes the maximum residual soil contamination level is uniformly present over the entire applicable vadose zone thickness appropriate to the  $K_d$  range (100:0 for  $K_d < 2$  mL/g, 70;30 for  $K_d \ge 2.0$  mL/g).

Peak concentrations in groundwater were calculated by running multiple simulations using STOMP for each constituent's  $K_d$  value. These results were used to calculate PRGs and SSLs for each constituent.

For the contaminants with higher  $K_d$  values, the peak concentration in groundwater within 1,000 years was less than 0.0001  $\mu g/L$  (for nonradionuclides) or less than 0.0001  $\mu g/L$  (for nonradionuclides) or less than 0.0001  $\mu g/L$  (for radionuclides) for most cases. In such cases, the PRG is assigned the code "NR" (non-representative condition), because peak groundwater concentrations this low are below a level of numerical significance. This threshold occurs at different  $K_d$  values for different soil columns and is highly dependent on the recharge scenario. This threshold therefore is different for SSL values based on the irrigation recharge scenario than for PRG values based on the native vegetation recharge scenario. It was therefore necessary to simulate a range of  $K_d$  values for each recharge scenario and each representative stratigraphic column to discern the applicable  $K_d$  threshold for which peak groundwater concentrations within 1000 years that were below 0.0001  $\mu g/L$  for nonradionuclides or below 0.0001  $\mu g/L$ 

The practical quantitation limit (PQL) for soil concentration for aroclors is 0.017 mg/kg. If the screening value or the PRG value for aroclors was calculated less than 0.017 mg/kg, then it was set to 0.017 mg/kg. The modeled PRG value selected for 100-D/H for Cr(VI) was calculated to be 21 mg/kg. The PRG value was subsequently constrained to a maximum value of 6 mg/kg because the  $K_d$  value used in the model

was derived from experiments with soil concentration less than 6 mg/kg. A PRG level of 2 mg/kg has been selected as the level used from the interim action ROD.

In the RI/FS process, waste sites are evaluated using PRGs. Known measured concentrations of COPCs are compared to the appropriate set of PRG values. If the concentration for one or more COPC exceeds either the groundwater-specific or surface water-specific PRG, then the site is carried into the FS, where options for addressing risks posed by the site will be determined and evaluated using the CERCLA criteria.

PRGs were determined for each COPC by simulating peak groundwater concentrations for all representative stratigraphic columns and surface soil types, assuming a particular recharge scenario and contaminant source distribution (either 100:0 or 70:30 model), and then selecting the smallest PRG value calculated from the resulting peak concentrations. Screening levels, which identified analytes to be designated as COPCs at each 100-D/H waste site, were determined in a similar manner to PRGs, but the irrigation recharge scenario was used in the SSL simulations to represent a maximum, reasonably foreseeable recharge condition for the future. This section summarizes the modeling approach for calculation of SSL and PRG values that are protective of both surface water and groundwater, describes their application, and identifies the underlying assumptions, conservatism, and uncertainties in the calculations. Calculation of a PRG or SSL is straightforward:

- A forward calculation to simulate variably saturated transport of a unit concentration of mass or
  activity of waste-derived COPCs from a specified interval in the vadose zone in which flow and
  solute transport are driven by a particular recharge scenario.
- Identify the peak groundwater concentration or activity resulting from forward calculation.
- A back calculation performed by dividing the peak into the potential ARAR (Chapter 8) or risk-based value for groundwater or surface water and correct for units to give the groundwater-specific or surface water-specific PRG or screening level, indicating the maximum soil concentration that would not result in an exceedance of the potential ARAR (Chapter 8).

This calculation process is repeated for different COPCs, recharge scenarios, and vadose zone geology representations. The most restrictive result from the range calculated for vadose zone geology representations is selected from the irrigation recharge scenario results for SSL values, and from native vegetation recharge scenario results for PRG values, for each COPC.

Calculation of PRG values for the 100-D/H source OU included the use of 1D numerical fate and transport simulations for some COPCs and scaling computations for the remaining COPCs. The STOMP code was selected to perform the simulations based on its ability to simulate the vadose zone features, events, and processes relevant to calculating PRGs in the 100 Area. In addition, STOMP was selected to satisfy the other code criteria and attributes identified in *Regulatory Basis and Implementation of a Graded Approach to Evaluation of Groundwater Protection* (DOE/RL-2011-50), which describes the basis for using STOMP in this type of evaluation.

#### 5.7.1 Identification of Peak Groundwater Concentrations

Peak groundwater concentrations were calculated along a portion of the domain's downgradient boundary corresponding to the top 5 m (16 ft) of the aquifer. The average concentration for the topmost 5 m (16 ft) was assumed a reasonable estimate of the groundwater concentration that would be measured within a 6 m (20 ft) long monitoring well screen that straddled the water table. The median hydraulic gradient for each area (100-D or 100-H) was applied across the saturated portion of the model domain to calculate the aquifer flux in the STOMP simulations. Thus, aquifer dilution is implicit in the calculation of peak

groundwater concentration. Median gradients were used as representative for each area because these were determined to be lower than the mean gradients; this therefore resulted in less dilution, and hence higher peak groundwater concentrations. The concentration was calculated in the aquifer beneath the downgradient edge of the footprint of a representative waste site (the point where the highest concentration would occur resulting from residual vadose zone contamination), from which the peak groundwater concentration of contaminant and breakthrough time were determined (*STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units* [ECF-HANFORD-11-0063] in Appendix F).

For reference, effective dilution factors that result from the STOMP models were calculated and presented for all combinations of recharge scenarios, recharge phases, and hydraulic gradients used in the alternative fate and transport modeling under steady-state conditions (see Table 9 in ECF-HANFORD-11-0063, in Appendix F). These dilution rates ranged from a low of 76 for the irrigation recharge rate at 100-D waste sites that have the saturated zone in the Ringold Formation, to a high of 15,600 for the mature shrub-steppe recharge rate at 100-H waste sites that have the saturated zone in the Hanford formation. For context, if the default fixed parameter three-phase partition model (WAC 173-340-747(3)(a)) were used to establish soil concentrations for groundwater protection, the default groundwater dilution factor is 20 for unsaturated zone soil. However, this default is not applicable to this calculation, because it uses an alternative fate and transport model (WAC 173-340-747(8)) and not the default parameter three-phase partition model. Where alternative fate and transport models are used, the WAC requires that dilution "be based on site-specific measurements or estimated using a model incorporating site-specific characteristics." This requirement is met in this calculation by using STOMP to model the aquifer with the appropriate aquifer thickness and a median hydraulic gradient based on site-specific measurements.

#### 5.7.2 Site-Specific Modeling

The graded approach for vadose zone modeling permitted application of site-specific modeling in cases where the individual waste site conditions were not adequately (conservatively) represented by the default SSL and/or PRG simulations) as described in Section 5.1. RI borehole profile data reported in Chapter 4 reveal instances of deep contamination (in the lower 30 percent of the profile) was present for higher  $K_d$  ( $K_d > 2 \text{ mL/g}$ ) COPCs, which may indicate that the 70:30 initial condition model for vertical contaminant distribution is non-conservative. However, it is also possible that the 70:30 initial condition model (which represents contamination as uniformly spread at a maximum level over the upper 70 percent of the soil column) still yields bounding SSL and PRG values because detection of contamination in the lower 30 percent of the soil profile doesn't necessarily result in higher SSL or PRG values. Prior to elevating these sites and these COPCs with deep vadose zone contamination detections to a site-specific modeling approach, a conservatism testing process was developed and used to evaluate whether any of the instances identified are within the bounding SSL and PRG values obtained from the bounding simulation approach. This "conservatism-testing" process, and results, is described here.

A comprehensive review of the RI borehole profile data reported in Chapter 4 was conducted to identify specific waste sites and specific higher sorption COPCs ( $K_d > 2$ ) that may not be conservatively represented by the 70:30 profile that was used to develop SSL and PRG values. The RI borehole profile data that exhibited concentrations of such higher  $K_d$  constituents were identified and then the list reduced to eliminate those cases that were as follows:

- From boreholes that did not sample the lower 30 percent of the vadose zone
- For COPCs for which there are no background values

- Reporting concentrations in the lower 30 percent of the vadose zone were within the range of background
- For COPCs with  $K_d > 25$  (the  $K_d$  threshold for which peak groundwater contamination does not exceed 0.0001 µg/L or 0.0001 pCi/L within 1000 years under the irrigation recharge scenario).
- For strontium-90

The reason for the exclusion of COPCs with  $K_d > 25$  was that results from vadose zone modeling to develop SSLs show that COPCs with  $K_d$  values higher than 25 result in NR values based on peak groundwater concentrations simulated within 1,000 years for the 100:0 profile; thus there is no need to evaluate these cases further. Strontium-90 was excluded because it was decided to assign the 100:0 profile to this constituent through the 100-D/H area based on its prevalence throughout the vadose zone in many locations, presence in groundwater, and recognition that this contaminant is a recognized risk driver in the 100 Area.

Based on the evaluation above, the following waste sites and COPCs were identified as potential cases for which the 70:30 profile may be non-conservative:

- 116-D-1A (trench), neptunium-237
- 116-D-7 (retention basin), antimony
- 116-DR-9 (retention basin), acenaphthene
- 116-H-1 (trench), phenanthrene
- 116-H-1 (trench), antimony
- 116-H-4 (pluto crib), antimony
- 116-H-6 (solar evaporation basin), antimony
- 116-H-7 (retention basin), antimony
- 116-H-7 (retention basin), molybdenum
- 118-H-6 (reactor fuel storage basin), neptunium-237

For each case on the above list, for purposes of testing the conservatism of the 70:30 profile, a single representative stratigraphic column (Figures 5-3 and 5-4) that most closely approximated the stratigraphy of the specific site being evaluated (from the list above) was chosen for detailed evaluation. This is in contrast to the generalized approach used to develop SSL and PRG values in which a range of representative stratigraphic conditions were simulated for selecting the most conservative result to bound all waste sites addressed. Simulations were performed in pairs: once with the actual vertical contamination profile reported in Chapter 4, and again using the 70:30 profile. The peak groundwater concentration predicted by the model were obtained from in each case in these pairs of simulations and compared. The conservatism of the 70:30 profile was considered validated if:

- 1. The simulated peak groundwater concentration obtained from observed contaminant distribution was less than the peak groundwater concentration obtained from the 70:30 profile.
- 2. The simulated peak groundwater concentration was less than the MCL for the constituent simulated.

The results of the above analysis for the identified sites and COPCs that were identified as potentially non-conservative revealed that the 70:30 profile was conservative in all instances; therefore no site-specific evaluations were required for establishing SSL and PRG values. The evaluation of the conservatism of the 70:30 profile is included in *STOMP 1-D Modeling for Determination of Soil* 

Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units (ECF-HANFORD-11-0063) in Appendix F.

#### 5.7.3 Comparison of Vadose Zone EPCs to SSLs and PRGs

The definition of, and process for identification of, COPCs is presented in Section 6.2.1.3. The EPCs of the residual contamination of COPCs for each waste site and soil group (for example, overburden, shallow, shallow focused, and deep) as indicated in the CVP data for the previously remediated waste sites are calculated through the process presented in Chapter 6 and summarized here. The EPC of each waste site and soil group is the UCL-95 of the mean concentration or the maximum detected if too few detections were available to estimate a UCL-95 value. The waste site-specific EPC of each constituent was compared to the model-derived SSLs protective of groundwater and protective of surface water in Comparison of 100-DR-1, 100-DR-2, 100-HR-1, and 100-HR-2 Source Operable Unit Exposure Point Concentrations to Soil Screening Levels Protective of Groundwater and Soil Screening Levels Protective of Surface Water (ECF-100DR1-11-0078), in Appendix F. No waste sites or constituents had EPCs that exceeded the groundwater protection or surface water protection SSLs in 100-D/H.

If a waste site soil group COPC EPC exceeded the model-derived SSL protective of groundwater or the model-derived SSL protective of surface water, then it was carried through to the second step for waste site assessment. The second step compares the EPCs of the COPCs that emerged from the screening level (SSL comparison) to model-derived PRGs protective of groundwater and surface water.

Recharge rates in 100-D/H would be greatest in the future under an irrigated agriculture land use. This land use is the basis for the screening analysis based on the irrigation recharge scenario defined for SSL derivation. The SSL represents the maximum constituent mass or activity soil concentration that will not result, under the irrigation recharge scenario, in a downgradient groundwater or surface water concentration exceeding the federal and state criteria listed in *STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units* (ECF-HANFORD-11-0063) in Appendix F.

Recharge rates in 100-D/H, as well as in the rest of the 100 Area, are expected to decrease after demolition and remediation activities are complete and the native xerophyte plant cover is reestablished under the reasonably anticipated land use of conservation. This is the basis for the native vegetation (that is, non-irrigated) recharge scenario defined for the PRG derivation. The PRG values represent the maximum constituent mass or activity soil concentration, under the native recharge scenario, that will not result in downgradient groundwater or surface water concentration exceeding the federal and state criteria listed in STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units (ECF-HANFORD-11-0063) in Appendix F.

There were no waste sites with SSL exceedances; therefore, no sites were screened against the PRGs. Human health and ecological screening is conducted as part of the risk assessment. The results of the SSL comparison are provided in *Comparison of 100-DR-1, 100-DR-2, 100-HR-1, and 100-HR-2 Source Operable Unit Exposure Point Concentrations to Soil Screening Levels Protective of Groundwater and Soil Screening Levels Protective of Surface Water* (ECF-100DR1-11-0078, Appendix F) for 100-D and 100-H waste sites. Uncertainties that may affect the interpretation of the comparison of site-specific EPCs to the SSLs and PRGs are discussed in Section 5.7.

#### 5.7.4 COPCs Retained for Assessment in Feasibility Study

As noted in the preceding subsection, no previously remediated waste sites exceeded screening levels, and none of those sites are carried into the FS. The waste sites that are not yet remediated are carried into the FS for evaluation, with the COPCs identified for those waste sites based on process knowledge.

#### 5.7.5 Evaluation of Special Consideration Sites

Six waste sites where the interim action excavation was performed into either the periodically rewetted zone and/or the saturated zone do not conform to the evaluation using the CSM for SSLs and PRGs above because the entire vadose zone was removed in the remediation. These waste sites are 100-D-8, 100-D-65, 100-D-66, 116-H-5, 128-H-1, and 132-H-3. These were identified for a site-specific evaluation for the following reasons:

- 128-H-1 burn pit, excavated below groundwater level; hence, the SSL/PRG model is not representative where clean backfill extends below the water table. However, verification samples from the sides of the excavation require evaluation to demonstrate groundwater and surface water protection standards are met by residual contamination at the edges of the excavated waste site. To demonstrate protectiveness, additional groundwater samples were collected from nearby monitoring and extraction wells. The results of the monthly or more frequent groundwater sampling indicated contaminant concentrations were below detection limits in most cases. Where contaminants were detected, levels decreased rapidly, and concentrations were below the maximum contaminant levels. It was determined that additional remediation was not warranted. Analytical data are included in the Remaining Sites Verification Package for the 128-H-1, 100-H Burning Pit Waste Site (May 2012), Appendix D.
- 132-H-3 effluent pumping station site, excavated below groundwater level; hence, the SSL/PRG model is not representative where clean backfill extends below the water table. However, verification samples from the sides of the excavation require evaluation to demonstrate groundwater and surface water protection standards are met by residual contamination at the edges of the excavated waste site.
- 116-H-5 outfall structure, river-shore site, excavated below river level; hence, the SSL/PRG model is not representative. Cleanup verification samples from the upland side of the excavation, above the river inundation level, require evaluation to demonstrate groundwater and surface water protection standards are met by residual contamination at the edges of the excavated waste site.
- 100-D-8 process sewer outfall site, near-river site; hence, the SSL/PRG model is not representative. Cleanup verification samples from the excavated surface, above the river inundation level, require evaluation to demonstrate groundwater and surface water protection standards are met by residual contamination at the edges of the excavated waste site.
- 100-D-65 process sewer outfall site, near-river site; hence, the SSL/PRG model is not representative. Cleanup verification samples from the excavated surface, above the river inundation level, require evaluation to demonstrate groundwater and surface water protection standards are met by residual contamination at the edges of the excavated waste site.

100-D-66 - process sewer outfall site, near-river site; hence, the SSL/PRG model is not representative. Cleanup verification samples from the excavated surface, above the river inundation level, require evaluation to demonstrate groundwater and surface water protection standards are met by residual contamination at the edges of the excavated waste site. A simplified conceptual representation was developed for these waste sites and evaluated using a STOMP 1-D model domain in ECF-HANFORD-11-0063 (Appendix F). This modeling resulted in bounding SSL and PRG values for the margins (edges) of the excavation that were compared to the soil samples collected at these margins. Groundwater SSL exceedances resulted in this evaluation (but no Groundwater PRG exceedances) for the

100-D-65 and 100-D-8 site (all for arsenic), but the SSL levels computed were all less than the Washington State and EPA cleanup standard of 20 ppm. Surface water SSL exceedances (but no surface water PRG exceedances) results in this evaluation for 100-D-65, 100-D-66, and 100-D-8 sites (for arsenic at 100-D-66 and for copper at all 3 sites). The same situation occurs for 116-H-5 and 128-H-1, where the only SSL exceedances were for arsenic, and all of the SSL values were less than the Washington State and EPA cleanup standard of 20 ppm.

### 5.8 Groundwater Contaminant Migration Assessment

The behavior of contaminants currently known to exist in groundwater at 100-D/H was evaluated using computer simulations to describe estimated future conditions. The approach to simulating groundwater contaminant migration and the technical basis for selecting specific input values are described in the following subsections.

#### 5.8.1 Factors Affecting Contaminant Mobility in the Saturated Zone

The transport velocity of contaminants in the saturated zone is dependent on the groundwater flow velocity and the specific retardation factor of each individual contaminant. The groundwater flow velocity, and hence the rate of contaminant transport, increases with increasing hydraulic conductivity and hydraulic gradients, yet decreases with increasing porosity. The retardation factor of contaminants in a given stratigraphic unit increases with increasing  $K_d$ . Each of these variables is dependent, in turn, upon other factors: historical discharges, natural recharge, artificial recharge (in this case, effluent disposal to trenches), sorption, groundwater treatment systems, and Columbia River stage variations. Discussion of each of these factors follows.

#### 5.8.1.1 Historical Discharges

Historical discharges are discussed here to provide insight into past and present groundwater conditions that contribute to the initial condition used as the starting point for groundwater modeling. Inferences regarding groundwater flow velocities and mound dissipation rates are explanatory, but are not direct inputs to the groundwater flow and transport model.

Site-related discharges of liquids and contaminants at 100-D/H entered the groundwater system at various times and locations during the historical operations at the OU. Low-concentration Cr(VI) and, periodically during upset conditions, low-concentration fission products entered the ground at locations of reactor cooling water discharge. These locations included leakage from the 116-D-7, 116-DR-9, and 116-H-7 Retention Basins, and direct discharges to the 116-DR-1&2 and 116-H-1 Trenches. These discharges resulted in the development of a large groundwater mound that extended for thousands of meters in all directions from the release points. The mound consisted primarily of discharged reactor cooling water that displaced the original groundwater. This groundwater mound would have exhibited a fairly uniform Cr(VI) content of about 700 µg/L, the concentration of that constituent in the working cooling water stream. This water stream likely also included various nonradiological contaminants associated with the cooling water treatment process, in addition to nuclear fuel and activation and fission products associated with periodic reactor fuel failures. The groundwater flow velocities associated with the cooling water mound during reactor operations at 100-D were measured at 3 m/day (10 ft/day) between the retention basins and the river. Across the Horn area (between 100-D and 100-H) the groundwater flow velocities were 10 m/day (30 ft/day). Groundwater flow velocity between the retention basin at 100-H and the river was measured at 6.1 m/day (20 ft/day). After cessation of cooling water discharges, the groundwater mounds rapidly subsided to near-natural groundwater elevations; however, the body of contaminated water was still in place and is presumed to have continued to migrate at slower, ambient groundwater velocities (Section 3.7.2) toward the Columbia River. Underlying 100-H, Cr(VI) in the

footprint of the former groundwater plume remains mobile; concentrations have decreased over that area since the implementation of the interim action pump-and-treat system in 1997.

Other historical releases to ground that apparently affected groundwater include spills and leaks of water treatment chemicals (including sodium dichromate dihydrate solution at high concentration, sodium hydroxide solution, sulfuric acid solution, sodium chloride solution, and alum solution [hydrated potassium aluminum sulfate]). These releases appear to have occurred over the operating period in or near the water treatment facilities at the D, DR, and H Reactors. French drains located near the bulk chemical receiving area at 100-D received spills and leaks. Numerous areas of chromium-stained vadose soil have been identified at both 100-D and 100-H as described in Section 4.2. The current groundwater plumes are a result of some of these releases reaching groundwater.

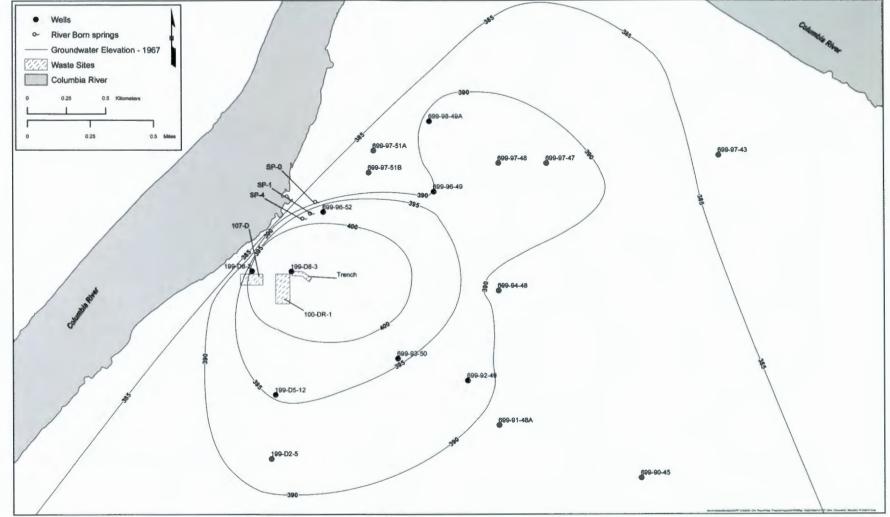
The 183-H sedimentation basins (originally part of the H Reactor cooling water treatment facilities) were removed from service at the end of reactor operations in 1965. In 1973, the eastern portion of the sedimentation basins were converted for use as an evaporation basin for waste generated in the 300 Area. Waste evaporation activities continued until 1985, when the remaining basin was closed. Groundwater monitoring at nearby wells indicates that contaminants from the evaporation operation entered groundwater soon after the operation commenced. Substantial concentrations of uranium, nitrate, sulfate, and sodium were observed in groundwater.

#### **5.8.1.2** Recharge

The recharge rate at 100-D/H has changed significantly from the period of reactor operations to current conditions. Large volumes of liquid wastes percolating through the vadose zone caused a mound in the water table in 100-D/H during operations. After the production ceased, the large-volume effluent disposal ended, and the hydraulic gradients began to return to natural conditions.

Groundwater recharge results from the net infiltration of precipitation, leaks, and liquid waste disposal. The high recharge rates present during operations affected groundwater elevations and resulted in changes in groundwater flow velocity and direction. During the operation of the D/DR Reactors, cooling water containing Cr(VI), other water treatment chemicals, and radionuclides was briefly held at leaking retention basins (*Status of the Ground Water Beneath Hanford Reactor Areas* [HW-77170]). An estimated combined leakage rate of 5,663,369 L/day (1,496,104 gal/day) resulted in mounding of the unconfined aquifer water table until February 1967 (Figure 5-6). An additional cause of recharge water unique to the source area remediation is the addition of water for dust suppression. Dust control water is applied at waste sites during excavation activities to minimize generation of fugitive dust that could expose workers or spread contamination beyond the work area. The goal of water application at work sites is to apply just enough to water to control fugitive dust without applying an amount that would have the potential to mobilize underlying vadose zone mobile contaminants. Achieving an optimum application rate is difficult due to heterogeneous soils, varying evapotranspiration potential, and constantly changing work surface configurations. Consequently, some water applied for dust control purposes can contribute to localized, elevated groundwater recharge rates for short periods during active remediation.





Source: Modified from BNWL-CC-1352, Ground Disposal of Reactor Cooling Effluent.

5-45

Figure 5-6. 107-DR Disposal Trenches 1 and 2 Infiltration Test Base Map and Initial Water-Level Distribution

#### 5.8.1.3 Effluent Disposal to Trenches

To evaluate the fate of effluent discharge to infiltration trenches and the associated effect on groundwater flow directions, an infiltration test was conducted between March and June 1967 (*Ground Disposal of Reactor Cooling Effluent* [BNWL-CC-1352]). During this test, 12,745,480,000 L (3,367,000,000 gal) of reactor coolant effluent were disposed to the joined 107-DR disposal trenches (116-DR-1&2 Trench). This is equivalent to approximately 141,616,500 L/day (37,400,000 gal/day), approximately 25 times the daily infiltration rate from the leaking retention basins and effluent lines (HW-77170). Hydrographs from wells near the infiltration area indicate that significant groundwater mounding occurred in response to the infiltration, and did not fully dissipate until 1968 to 1969 although it was largely gone by September 1967 (Figure 5-7). A detailed discussion on this infiltration test is presented in Chapter 3, Section 3.7.1.

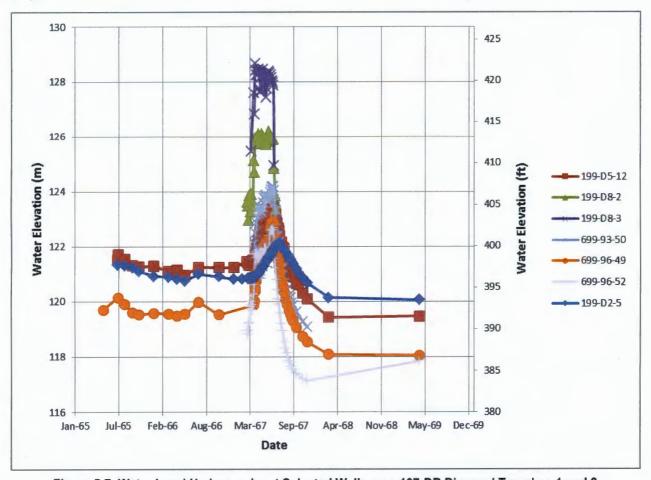


Figure 5-7. Water Level Hydrographs at Selected Wells near 107-DR Disposal Trenches 1 and 2

To characterize the extent of mounding created by the infiltration test and to evaluate its effect on flow direction and potential contaminant migration pathways, an analysis was undertaken as part of this RI/FS to accomplish the following:

- Map groundwater levels measured during and after the infiltration test.
- Evaluate the resulting pattern of hydraulic gradients and resulting groundwater flow directions during each of these periods.

To accomplish this, groundwater levels that were measured in monitoring wells every few days during and after the infiltration test were compiled. Groundwater levels were converted to elevations and

placed on a map using a water-level mapping technique that incorporates mounding in response to injection of water (Collection and Mapping of Water Levels to Assist in the Evaluation of Groundwater Pump-and-Treat Remedy Performance [SGW-42305]). This technique combines universal kriging of the groundwater levels with a linear trend and an additional term to account for aquifer response to infiltration at a point source of water.

Because the Columbia River influences groundwater elevations, an estimate of the river stage throughout the infiltration test period was required to construct the groundwater level maps. Although groundwater level data are available throughout the period of interest, only recent river stage data are available. To obtain estimated river stage elevations throughout the period of interest, an empirical function was developed for each river gauge location by developing a correlation between daily river gauge values for the period 2006 to 2009 and daily average dam discharge rates from the Columbia River gauge below Priest Rapids Dam for the same period. This empirical function was then used to calculate an approximate river stage at each river gauge for each event on which groundwater levels are available during the period of the infiltration test. Linear interpolation between the river gauge water level estimates provided a continuous estimate of the river stage along the shoreline for inclusion in the groundwater level mapping.

Semi-annual groundwater level maps were prepared using combined groundwater levels and river stage data. Two examples of groundwater level maps are provided on Figure 5-8, illustrating approximate groundwater flow patterns during and at some time following the infiltration test. The analysis suggests that substantial mounding had developed during reactor operations before the infiltration test. The infiltration test caused further mounding, which resulted in an increase in the hydraulic gradient and groundwater flow velocity across the Horn area. Maps reflecting conditions during the infiltration test (such as Figure 5-8, inset 1), and for the time following operations until mounding dissipated, indicate that the infiltration of effluent water provided a mechanism to transport contaminants at relatively low concentrations inland of source areas associated with the D Reactor, and across the Horn area toward the H Reactor, under conditions of both high and low river stage. Similar but lesser effects would be expected to have occurred because of leakage from the retention basins. Groundwater level maps that were prepared using data obtained sometime after the cessation of operations and the infiltration test (such as Figure 5-8, inset 2) suggest that migration from the D Reactor toward the H Reactor may occur under current conditions during times of high river stage. However, at times of low river stage, migration would be primarily toward the Columbia River as discussed in Section 3.7.2.

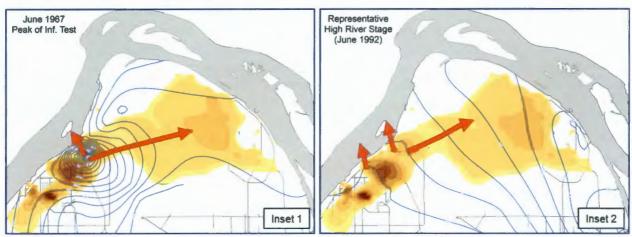


Figure 5-8. Groundwater Level Distributions and Potential Plume Migration Pathways due to the 100-D Trench Test

#### 5.8.1.4 Sorption

Tritium, nitrate, and sulfate are highly mobile ( $K_d = 0 \text{ mL/g}$ ; Table 5-4) and migrate at the same velocity as groundwater under ambient geochemical conditions. Cr(VI) is considered moderately mobile ( $0 \text{ mL/g} < K_d \le 1 \text{ mL/g}$ ) in 100-D/H groundwater. Strontium-90 in 100-D/H groundwater is a divalent cation and is considered slightly mobile (in range  $1 < K_d < 30 \text{ mL/g}$ ; in the case of strontium-90, 25 mL/g) in near-neutral or slightly basic groundwater. Chloroform is a moderately mobile ( $0 \text{ mL/g} < K_d \le 1 \text{ mL/g}$ ) chlorinated solvent. Cr(VI) is assumed to exhibit a  $K_d$  of zero in the groundwater transport simulations. Sorption is simulated using a dual-domain (mobile/immobile) formulation presented below in Section 5.8.2.2; the specific  $K_d$  values used in each domain for that formulation are provided in that section.

#### 5.8.1.5 Groundwater Treatment Systems

The 100-D/H pump-and-treat systems are described in detail in Chapter 1. The 100-HR-3 pump-and-treat system began operating in 1997. The 100-DR-5 system was added in 2007. The 100-DX system began operating in 2010. The 100-HX system began operating in 2011. Note that the 100-HR-3 and DR-5 systems are no longer operational since the 100-DX/HX systems came online. The 100-DX/HX pump-and-treat system was installed to expand the area of influence and to increase the capacity of the treatment system to 1,400 gpm. The systems are operated to intercept Cr(VI) before it reaches the Columbia River, with the objective of limiting concentrations of Cr(VI) at concentrations that do not exceed the 10  $\mu$ g/L AWQC. The estimated future effects of pump-and-treat operations under selected scenarios are discussed in the FS portion of this report.

The capture efficiency of these systems was evaluated using a numerical groundwater flow model. The modeling approach and the results of the evaluation are presented later in this report.

The ISRM barrier discussed in Chapter 1 was installed to chemically reduce dissolved Cr(VI) in groundwater to the essentially immobile ( $K_d > 30 \text{ mL/g}$ ) and less toxic Cr(III) species. The barrier was constructed by injecting sodium dithionite with potassium carbonate and potassium bicarbonate pH buffers with the purpose of creating a residual reduced zone within the aquifer that would provide ongoing removal of Cr(VI) from groundwater. The ISRM barrier has exhibited variable performance. The barrier has been supplemented by extraction wells and an ex situ treatment system in the highest concentration portion of the plume to prevent it from extending to the Columbia River.

#### 5.8.1.6 Columbia River Stage Variations

As discussed in Chapter 3 (Section 3.3.1), the Columbia River is a discharge boundary for the aquifer system, and the unconfined aquifer is in direct communication with the river along the shoreline of 100-D/H. Changing river stage influences groundwater elevations several hundred meters inland, but with diminishing influence at increasing distance from the river. At the river, high river stage can be more than 3 m (10 ft) higher than low river stage. Groundwater elevations have varied by up to 1.0 m/day (3.3 ft/day) in some wells nearest the river and up to approximately 1.8 m (6 ft) over the season in a few wells. This results in the PRZ being largest for sites nearest the river and smaller with increasing distance from the river. During high river stages, the inland flow direction in areas near the river and the reduced hydraulic gradients in more inland areas reduce the annual net groundwater flow velocity toward the Columbia River and the migration rate of contaminants dissolved in the groundwater. Groundwater in the Horn area appears to be more dramatically influenced by high river stage conditions; the groundwater flow direction appears to move directly from the river on the upstream side of the Horn area into the aquifer and move toward the downstream side of the Horn area near the 100-H Area.

#### 5.8.2 Saturated Zone Modeling Methods

A groundwater flow and contaminant transport model has been developed and calibrated for purposes of remedy design evaluation in the 100 Area. The model development and calibration was comprehensively documented in Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model (SGW-46279) in Appendix F. The groundwater flow model was constructed using the U.S. Geological Survey (USGS) modular groundwater flow model, MODFLOW ("A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model" [McDonald and Harbaugh, 1988]). Particle tracking was performed using the USGS program, MODPATH (User's Guide for MODPATH/MODPATH-PLOT, Version 3: A Particle Tracking Post-Processing Package for MODFLOW, the U.S. Geological Survey Finite-Difference Ground-Water Flow Model [Pollock, 1994]). The modular 3D multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems (MT3DMS) was used to simulate the contaminant plume migration (MT3DMS: A Modular Three-Dimensional Multi-Species Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems; Documentation and User's Guide [Zheng and Wang, 1999]).

The potential to apply historical concentration data, particularly tritium, to support inverse calibration of the groundwater model was considered. The available data were judged inadequate to this purpose, because only trailing edge behavior was available. Hence, these data are of limited value to calibrate a numerical flow and transport model.

A summary description of the model development and deployment is presented below. Additional details are presented in *Modeling of RI/FS Design Alternatives for 100-HR-3* (ECF-100HR3-11-0114) in Appendix F.

#### 5.8.2.1 Model Structure

The finite difference grid for the groundwater flow model encompasses all 100 Area OUs. The grid is constructed so that the northwest and northeast boundaries of the flow model parallel and abut the Columbia River. The model extends southward, toward Gable Butte and Gable Mountain. The grid spacing is relatively coarse (about 100 m [328 ft]) throughout much of the domain, but it is refined (15 m [49 ft]) near each 100 Area OU to support remedy evaluations.

Groundwater flow is simulated as 3D using four layers. These layers represent the Hanford formation (always present in Layer 1, across the model domain) and the Ringold Formation unit E (typically represented by Layers 2 through 4, except east of 100-D where it is absent and therefore all model layers represent the Hanford formation). Throughout much of the western half of the modeled area (including 100-K and 100-D), the water table lies within the Ringold Formation unit E sands, whereas toward the east and north of the modeled area (including 100-H and 100-F), the water table lies within the Hanford formation sands and gravels. Near 100-BC, the water table fluctuates between the two formations.

The base of the model was set as the top of the RUM where present and the top of the basalt where the RUM is absent, which typically occurs in the southern portions of the model approaching Gable Butte. The geologic characterization was compiled as part of the model data packages (100-HR-3 Remedial Process Optimization Modeling Data Package [SGW-40781]; 100-KR-4 Remedial Process Optimization Modeling Data Package [SGW-41213]; Geohydrologic Data Package in Support of 100-BC-5 Modeling [SGW-44022]; Geohydrologic Data Package in Support of 100-FR-3 Modeling [SGW-47040]). This characterization depicts the lateral facies transition from Ringold Formation unit E in the west and south of the model domain, to the Hanford formation sands and gravels in the east and north of the model domain, between 100-D and 100-H. Some of these model data packages have been revised since use in model construction; these revisions included updated and new information on hydrogeology, aquifer

properties, water-level maps, river data and bathymetry, and aquifer tubes and chromium concentration along the river shoreline. However, the transition from Ringold Formation unit E to the Hanford formation did not change in these revisions.

The establishment of the initial plume condition for the simulation was intended to describe an approximation of the current contaminant distribution and applied a conservative approach. Contaminant measurements at individual monitoring wells were distributed uniformly across the model layers at measurement locations. Subsequent transport simulations allow for movement of contaminants between the layers in the saturated zone. The model domain of the saturated zone is subject to contaminant distribution uncertainty because of variability in actual well construction and screen placement. The placement of contaminants across the full thickness of the aquifer in the initial condition is expected to be conservative in light of vertical profile measurements that indicate actual substantial variation in vertical contaminant distribution.

The principal aquifer property specified in the flow model is the spatially varying hydraulic conductivity of the saturated aquifer materials. The hydraulic conductivity distribution in the model was developed based on the information included in the model data package and a pilot-point approach implemented in the model calibration process. Estimates of hydraulic conductivity compiled as part of the model data package were tabulated and assigned to their corresponding aquifer unit. The values for the aquifer hydraulic conductivity that resulted from the model evaluation process are 19 m/day (62 ft/day) for Ringold Formation unit E in 100-D and 63 m/day (206 ft/day) for the Hanford formation. Hydraulic parameters used in the model to support the calibration were based on recent characterization data (variable hydraulic conductivity and fixed specific yield and specific storage parameters); these are documented in *Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model* (SGW-46279) in Appendix F. The 100 Area Groundwater Model was calibrated to water level data from 94 monitoring wells for the period January 2006 to June 2009. In total, 10,441 water level measurements were tabulated for the calibration process.

Natural recharge resulting from precipitation was specified based on information included in *Groundwater Data Package for Hanford Assessments* (PNNL-14753). An electronic version of the recharge package developed in that report was obtained, and the data were spatially distributed to the model grid cells and then adjusted during the model calibration process. Based on the results of the model calibration process, the recharge value was set equal to 12 mm/yr throughout much of the model domain.

The natural recharge rate applied to the groundwater model (12 mm/yr) is consistent with the natural recharge rates applied for vadose zone simulations to develop SSLs and PRGs (Table 5-7) because this rate represents a spatial average of recharge rates applicable to the extent of the groundwater model domain. The mean recharge rate applied for the groundwater model is applicable to the large area represented by that model (encompassing all of the 100 Area), which includes substantial variability in land surface soil types and vegetation cover. The 100 Area Groundwater Model domain extent is estimated (based on normalized difference vegetation index [NDVI]satellite data) to include approximately 87 percent vegetated land cover, and 13 percent non-vegetated land cover. The spatial average of applicable recharge rates (assuming 4.0 mm/yr for vegetated areas and 63 mm/yr for non-vegetated areas) is approximately 12 mm/yr. This rate is applicable to the upper boundary of this large spatial model, encompassing the entire 100 Area, for present-day conditions that are assumed to persist as a constant condition for approximately 100 years (the simulation period of the groundwater model). In contrast, the recharge rates applied for vadose zone model apply to a smaller, local-scale waste site. Recharge rates applied to the vadose model are assumed change over time following the assumptions of the recharge scenarios applied (irrigation or native vegetation) and are applied for a significantly longer period (1000 years). For present day conditions (bare soil), the recharge rates for waste sites is 63 mm/yr

(see Table 5-7 for recharge rates under bare soil, 2010–2015). The groundwater model surface area averages recharge from these bare soil areas (e.g., waste sites at present) with larger areas of native vegetation cover with recharge rates ranging from 1.5 to 4.0 mm/yr (see Table 5-7 for recharge rates under mature shrub-steppe native vegetation cover, after 2045). Thus, the 12 mm/yr rate is consistent when considered in context as a spatially averaged value over diverse land cover conditions during the model simulation period.

Anthropogenic recharge applied in the 100 Area Groundwater Model is summarized in the model package report (*Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model* [SGW-46279] in Appendix F) and for the 100-D and 100-H Areas, leakage events identified since 2000 are confined to the 182-D reservoir, in 3 distinct events.

Effective porosity and specific yield values for the entire aquifer were identified from published sources and revised during the model calibration and are equal to 18 and 10 percent, respectively. Both values are within the range of values documented in previous investigations for the Hanford Site (*Development of a Three-Dimensional Ground-Water Model of the Hanford Site Unconfined Aquifer System: FY 1995 Status Report* [PNL-10886]). Riverbed conductance values were also determined during calibration, separately for the stretches of the Columbia River within each area, to reflect the variability in geologic conditions in each area.

The groundwater flow model was calibrated to data included in the model data packages for each OU, through a combined manual and automated process. The model calibration was facilitated by using the parameter estimation software program (PEST) (*User's Manual for PEST Version 11* [Doherty, 2010]) and post-processing programs that calculate water level responses to stresses. The model was calibrated to data from January 2006 to December 2010. Calibration focused on the transient response of water levels to transient pumping and river stage stresses, and how these compare to values measured at wells at each OU. In addition, maps of water level contours calculated by the model were compared to contours included in published reports to ensure that the simulated hydraulic gradient magnitude and direction agree with prior independent interpretations.

A summary of the calibration statistics for the 100 Area Groundwater Model, as a whole, and within the 100-D and 100-H Areas, is provided in Table 5-8. The ratio of the Root Mean Squared Error (RMSE) to the range of the measured values is 1.96 percent: a ratio of less than ten percent is often used as one line of evidence to support a satisfactory calibration. However, in such a dynamic environment as the Hanford Site river corridor, visual comparison of simulated and measured data using scatter plots, frequency plots and hydrographs is perhaps the most suitable means for evaluating how well the model reproduces the observed groundwater response. The correspondence between measured and calculated water levels is illustrated with a scatterplot in Figure 5-9. A cumulative frequency chart of the residuals is illustrated in Figure 5-10. This chart summarizes the distribution of residuals for the entire model. The residuals are normally distributed about a value of 0.24 m.

Table 5-8. 100 Area Groundwater Model Calibration Statistics Summary

Metric	100 Area	100-D	100-H
Coefficient of Correlation	0.97	0.92	0.88
$\mathbb{R}^2$	0.95	0.85	0.77
Average Residual (m)	0.24	0.25	0.05
Maximum Residual (m)	11.19	1.14	1.36

Table 5-8. 100 Area Groundwater Model Calibration Statistics Summary

100 Area	100-D	100-H
-1.53	-0.45	-0.31
1993.6	582.7	127.9
0.66	0.57	0.50
0.44	0.33	0.25
22.35	3.27	3.24
1.96	10.04	7.77
	-1.53 1993.6 0.66 0.44 22.35	-1.53 -0.45 1993.6 582.7 0.66 0.57 0.44 0.33 22.35 3.27

Source: Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model (SGW-46279), Table 6-1; Appendix F.

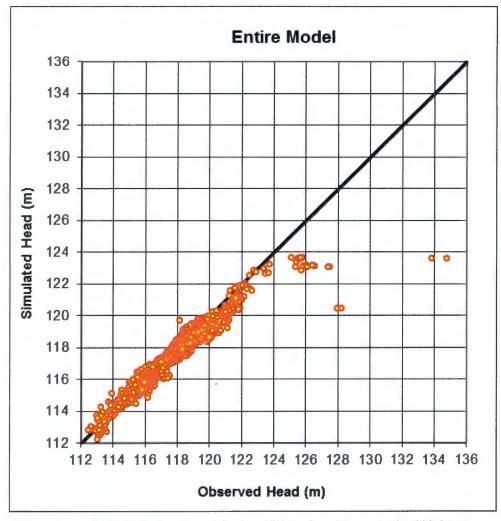


Figure 5-9. Measured versus Calculated Water Levels across the 100 Area Groundwater Model Domain

Further details about all parameter values used in the model are included in the comprehensive modeling report (*Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model* [SGW-46279 in Appendix F]).

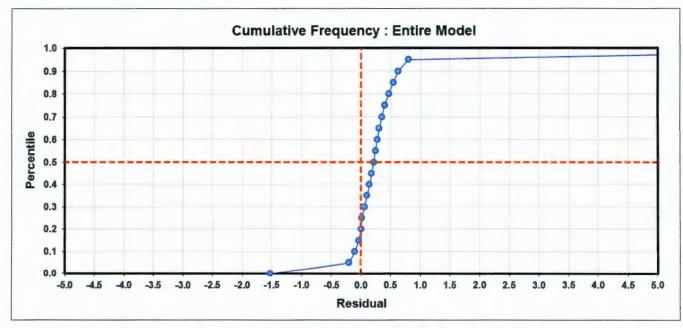


Figure 5-10. Cumulative Frequency of the Water Level Residuals across the 100 Area Groundwater Model Domain

## 5.8.2.2 Contaminant Transport Processes

The migration of Cr(VI) in response to current and projected extraction and injection well operations in 100-D/H was simulated to support remedy design evaluation; total chromium is anticipated to follow similar patterns. In addition to modeling of Cr(VI), transport simulations were performed for strontium-90 and nitrate to evaluate corresponding migration patterns because of the current and projected extraction and injection well operations. Transport simulations were based on the following:

- Transient flow fields calculated by the groundwater flow model
- · An initial distribution for each COC in groundwater
- A dual-domain formulation representing plume migration in a dual-porosity continuum with mass transfer between the mobile and immobile domains

The dual-domain concept applies multiple  $K_d$  values to the migration of selected contaminants to better describe their overall observed migration. For example, a highly mobile contaminant that typically exhibits a  $K_d$  of 0 may be assigned a small  $K_d$  value for a portion of the aquifer system. This small  $K_d$  reflects a migration retardation effect that may actually result from any of a number of physical processes, ranging from ionic exchange to retention of dissolved contaminants within low-permeability portions of the aquifer. The dual-domain approach is used to address some of the uncertainty in contaminant transport estimates when exact parameter values are not well known and observed contaminant behavior suggests that actual migration is variable.

Nitrate and strontium-90 passing through the ion exchange treatment system are not removed under the current treatment process. They are therefore recirculated in the aquifer via injection at the injection wells connected to each treatment plant. Nitrate and strontium-90 concentrations injected back into the aquifer are equal to the blended influent concentration at the treatment plant. The regulations in WAC 173-218, "Underground Injection Control Program," and 40 CFR 144, "Underground Injection Control Program," Subpart B, "General Program Requirements," prohibit the use of an injection well that may result in a violation of any primary drinking water standard or that may otherwise adversely affect beneficial use of groundwater. The treated groundwater being injected would not contain any constituents at a

concentration exceeding drinking water standards, and beneficial use of the groundwater would not be affected. WAC 173-218, "Underground Injection Control Program," prohibits certain discharges to groundwater; however, this regulation specifically excludes cleanup actions undertaken pursuant to CERCLA.

Recent studies by PNNL (such as *Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site* [PNNL-17674]) suggest (based on a series of column and batch experiments to investigate Cr(VI) mobility during advective transport under saturated conditions) that Cr(VI) within the vadose zone of the 100 Area exhibits migration characteristics that may be more complex than can be represented using simple advection. According to these tests, although the majority of the mass is highly mobile and migrates by advection, Cr(VI) mass can be held in heterogeneous parts of the aquifer of low hydraulic conductivity. This immobile Cr(VI) constitutes a longer-term continuing source to the mobile domain, facilitated by mass transfer between the domains. Based on these observations, the migration of Cr(VI) can be described by a dual-domain (or dual-porosity) approach that divides the aquifer into two domains: the mobile and immobile, using the bimodal grain-size distribution noted in Chapter 3. Advective transport occurs predominantly in the mobile domain, while mass transfer occurs by diffusion between the mobile and immobile domains.

MT3DMS, which is discussed in detail in the modeling analysis (*Modeling of RI/FS Design Alternatives for 100-HR-3* [ECF-100HR3-11-0114]), supports the use of a dual-domain formulation to simulate the transport of a contaminant in groundwater. The following parameters must be specified for the dual-domain formulation: the fraction of mobile and immobile domains; the mass transfer coefficient between the mobile and immobile domains; and K<sub>d</sub> describing sorption within the mobile and immobile domains. For the 100 Area transport model, it was assumed that for Cr(VI) sorption occurs within the immobile domain, and that no sorption occurs within the mobile domain. Sorption occurs both in the mobile and immobile domain for strontium-90. No sorption was assumed for nitrate, which was simulated using a single-domain, single-porosity formulation. The parameter values for the dual-domain formulation for transport simulation are listed in Table 5-9. Further details on the development of the dual-domain parameters can be found in *Modeling of RI/FS Design Alternatives for 100-HR-3* (Appendix F; ECF-100HR3-11-0114) and in the comprehensive modeling report (*Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model* [SGW-46279]; Appendix F).

Table 5-9. Parameter Values for the MT3DMS Transport Simulations

	Chromium		Nitrate	Strontium	
Parameter	Mobile Domain	Immobile Domain	Single Domain	Mobile Domain	Immobile Domain
Porosity	0.18	0.045	0.225	0.18	0.045
Bulk density (g/cc)	1.72		1.72	1.72	
K <sub>d</sub> (cc/g)	$0.0^{a}$	0.3	-	7.0 <sup>b</sup>	39.0 <sup>b</sup>
Decay in water (1/day)	0.0		-	6.59E-05	
Decay on soil (1/day)	0.0		-	6.59E-05	
Radioactive Decay Half-life (years) <sup>c</sup>			-	28.8	
Mass transfer rate (1/day)	0.01		-	0.01	

Table 5-9. Parameter Values for the MT3DMS Transport Simulations

	Chromium		Nitrate	Strontium	
Parameter	Mobile Domain	Immobile Domain	Single Domain	Mobile Domain	Immobile Domain

a. PNNL-18564, Table 6.9, sandy gravel sediment type.

Radioactive decay was considered for strontium-90 ( $T_{1/2} = 28.8$  years).

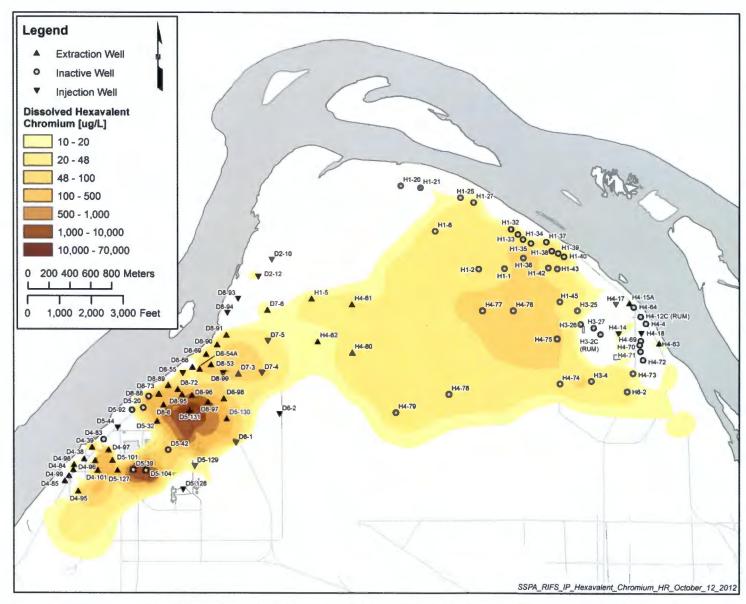
#### 5.8.2.3 Contaminant Initial Conditions

Initial conditions for the COCs in groundwater within the 100-D/H were obtained based on average sampled COC concentrations within the fall 2011 timeframe (discussed in Chapter 4) at each monitoring location as reflected on the plume depictions presented in Hanford Site Groundwater Monitoring for 2011 (DOE/RL-2011-118, Section 2.5). Concentrations tend to be highest at the low river stage that coincides with fall for this reach of the Columbia River. For nitrate and strontium-90, these plumes represent an annual composite of data collected throughout the calendar year. There is unlikely to be a seasonal variation in the strontium-90 plume. Nitrate concentrations fluctuate slightly, as discussed in 100-H (Section 4.5.2). For Cr(VI), the plume depiction for Fall 2011 was used (plumes were provided in DOE/RL-2011-118 for April to June timeframe and for October to December timeframe; these are shown in Figures 1-24 and 1-25 of this document), although it was noted the plumes were similar in these periods. Contaminant data are not collected from all wells on a single date. Therefore, it is necessary to develop initial contaminant conditions from samples collected from monitoring wells over a period: in this case, annual plume maps for nitrate and strontium-90, and the fall plume map for Cr(VI). It was noted in DOE/RL-2011-118 that the fall and spring Cr(VI) plumes were similar, both with an overall area above 20 μg/L of about 7 km<sup>2</sup>. These maps, which were derived from average concentration readings for their respective periods, are used to estimate the initial condition at a single point in time, in this case, the start of January 1, 2011. This time-aggregated estimate is then used to represent the initial condition from which the model commences transport simulation at a designated start time. The initial Cr(VI) distribution in the 100-HR-3 OU is shown on Figure 5-11. Figures 5-12 and 5-13 show the resulting distributions for strontium-90 and nitrate, respectively. Note that solid triangles in these figures depict pump-and-treat wells, pointing up for extraction wells and pointing down for injection wells. Open circles are used on the figures to depict inactive wells at a given time. Therefore, these figures show most of the wells near 100-H as inactive because they did not enter service until the 100-HX system became operational in October 2011. The wells used for the old 100-HR-3 system were still active in January 2011. In later figures that represent 2012, these wells will be depicted as triangles pointing in the appropriate direction as the systems are turned on later in 2011 and shut down at the end of 2012.

The initial condition shown in Figure 5-13 for nitrate depicts two elevated nitrate concentration areas (plumes) near Wells H4-75 and H1-27. These plumes were reported in the source used for development of this initial nitrate condition (DOE/RL-2011-118, Section 2.5), but these plume depictions were subsequently investigated and determined to be based on erroneous data; a revised depiction of current nitrate conditions is provided in Figure 4-90. Modeling was not repeated for nitrate to correct for these non-existent nitrate plumes because predictive simulations did not indicate these would lead to a need for action.

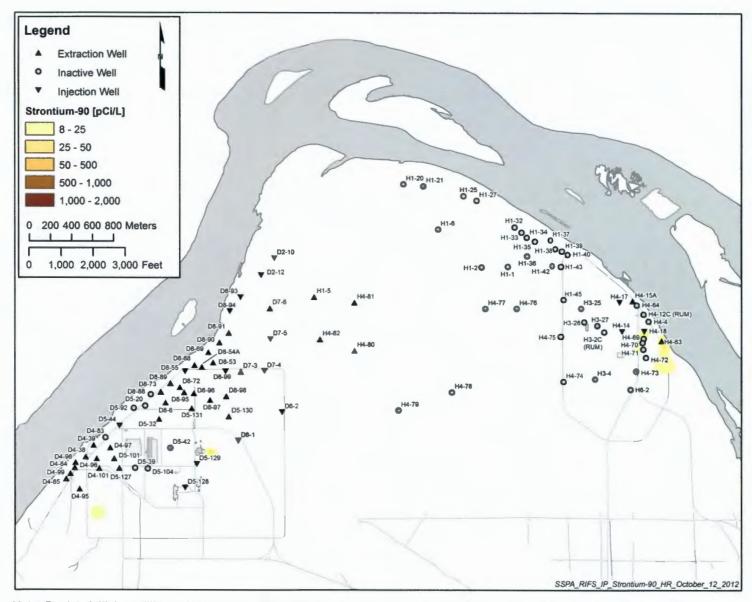
b. Based on a value of 12 cc/g (PNNL-18564, Table 6.9, Sandy Gravel sediment type) and distributed in the mobile and immobile domains based on the approximate ratio of the corresponding porosities.

c. Decay values in water/soil correspond to the half-life represented by the radioactive decay.



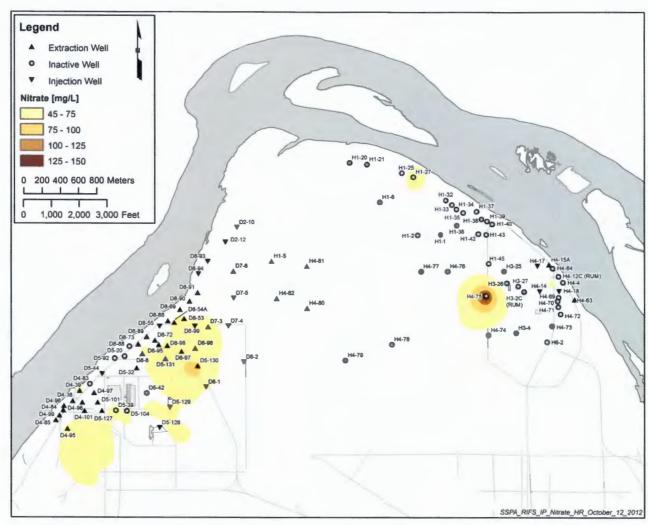
Note: Depicts initial condition of the Cr(VI) contaminant plume in the groundwater transport model representing conditions at start of January 1, 2011.

Figure 5-11. 100-DX/HX Pump-and-Treat Well Configuration and Approximate Extent of Dissolved Cr(VI) in 100-D/H



Note: Depicts initial condition of the strontium-90 contaminant plume in the groundwater transport model representing conditions at start of January 1, 2011.

Figure 5-12. 100-DX/HX Pump-and-Treat Well Configuration and Approximate Extent of Strontium-90 in 100-D/H



Note: Depicts initial condition of the nitrate contaminant plume in the groundwater transport model representing conditions at start of January 1, 2011.

Note: The elevated nitrate concentration areas evident near wells H4-75 and H1-27 were reported in the source used for development of this initial nitrate condition, but these plume depictions were subsequently investigated and determined to be based on erroneous data; a revised depiction of current nitrate conditions is provided in Figure 4-90. Modeling was not repeated for nitrate to correct for these non-existent nitrate plumes because predictive simulations did not indicate these would lead to a need for action (see Figures 5-28 through 5-31.

Figure 5-13. 100-DX/HX Pump-and-Treat Well Configuration and Approximate Extent of Nitrate in 100-D/H

# 5.8.3 Model Deployment

The groundwater flow and transport model was used to simulate flow conditions and Cr(VI), strontium-90, and nitrate plume migration patterns, assuming the reported operation of the interim pump-and-treat system in the 100-HR-3 OU during 2011–2012, which includes the 100-DX and 100-HX treatment plants and the associated extraction and injection wells. *Modeling of RI/FS Design Alternatives for 100-HR-3* (ECF-100HR3-11-114), Table 3-2 (Appendix F) includes a list of all pump-and-treat wells with their corresponding pumping rates. The base case is comprised of a "no further action" simulation in which pump-and-treat extraction and injection wells were assumed to end operation at the end of CY 2012, and ambient flow conditions persist thereafter. The model input parameters are summarized in Table 5-10 for this no further action case.

Table 5-10. Summary of Selected Primary Fate and Transport Simulation Input Parameters Used with Groundwater Flow and Transport Model Implemented in the MODFLOW and MT3DMS Codes for in the 100-HR-3 Groundwater Operable Unit<sup>a</sup>

Input Parameter (units)	Input Parameter Value			
Simulation Duration				
Simulation of historical conditions (used for model calibration)	5 years – January 2006 through December 2010 Monthly stress periods			
Simulation of future conditions	77 years – January 2011 through December 2087  Monthly stress periods for first 27 years (January 2011 through December 2037) followed by a single stress period of 50 years (January 2038 through December 2087) using average stage conditions represented by January data			
	Upper Boundary Condition: Recharge			
Recharge Boundary	Recharge values reported in PNNL-14753, <i>Groundwater Data Package for Hanford Assessments</i> , were uniformly scaled during the model calibration process to provide improved fit to measured groundwater elevations. Resulted in a "typical value" for groundwater recharge of 12 mm/yr <sup>b,c</sup> throughout the model domain.			
	Lateral Boundary Conditions			
Constant Head Boundaries	Used to represent time-variant hydraulic head distribution in model cells representing a) the Western Gap and b) the Gable Gap.			
General Head Boundaries	Used to represent flow into and out of the model domain along a) the southeast model boundary between Gable Mountain and the Columbia River, and b) the western boundary of the model. Stress-period specific, spatially variable values specified on the basis of a map of sitewide groundwater elevations representing typical groundwater level condition in 2006–2010.			
River Boundary	River stage data from six gauges located near each Operable Unit plus USGS Gauge 12472800 (located below Priest Rapids Dam) were processed and summarized to monthly average stage values for application in each stress period.			

Table 5-10. Summary of Selected Primary Fate and Transport Simulation Input Parameters Used with Groundwater Flow and Transport Model Implemented in the MODFLOW and MT3DMS Codes for in the 100-HR-3 Groundwater Operable Unit<sup>a</sup>

Input Parameter (units)	Input Parameter Value		
	Lower Boundary Condition	1	
No Flow Boundary	The lower boundary of the model is a no-flow boundary, in keeping with the stratigraphy selected to choose relatively impermeable units (aquitard, basalt, or mud) to serve as the lower boundary.		
	Sources and Sinks		
Pumping Stresses	No-Further-Action Scenario <sup>d</sup> :  • January 2006 through December 2012: extraction and injection rates for 100 Area pump-and-treat systems included for the following systems: DR-5, HR-3, DX, HX, KX, KR4, and KW.  • After December 2012: no further pumping.		
	Hydraulic Parameters		
Specific yield (unitless)	0.10 <sup>a,e</sup>		
Specific storage (1/day)	$0.000005^{a,f}$		
	Hanford formation	Ringold Formation	
<i>K<sub>h</sub></i> saturated horizontal hydraulic conductivity (m/d)	Spatially variable; mean zonal value in: 63 <sup>b</sup>	Spatially variable; mean zonal value in: 19 <sup>b</sup>	
Vertical anisotropy ratio $(K_{\nu}/K_h)$	0.1		
	Transport Parameters		
Total porosity (unitless)	0.225		
Mobile porosity (unitless)	0.18		
Immobile porosity (unitless)	0.045		
First-order dual-domain mass transfer rate (1/day)	0.01		
$\rho_b$ bulk density (g/mL)	1.72		
$\alpha_L$ longitudinal dispersivity (m)	0 (dispersivity neglected; conservative assumption with regard to peak concentration)		
$\alpha_T \alpha_L$ dispersivity anisotropy ratio (dimensionless)	N/A (longitudinal dispersion neglected)		
$K_d$ distribution coefficient (mL/g)	Contaminant-dependent and modeled using dual-domain approach; see SGW-46279 and ECF-100HR4-11-0114 in Appendix F for details.		

Table 5-10. Summary of Selected Primary Fate and Transport Simulation Input Parameters Used with Groundwater Flow and Transport Model Implemented in the MODFLOW and MT3DMS Codes for in the 100-HR-3 Groundwater Operable Unit<sup>2</sup>

### **Input Parameter (units)**

#### **Input Parameter Value**

- a. Details on the basis for all parameters in this table are found in Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model (SGW-46279) in Appendix F.
- b. Denotes calibrated value.
- c. Recharge rate represents an average over a large area represented by the groundwater model with spatially distributed surface soil types and vegetative cover under present day conditions. This value is not directly comparable to recharge rates applied for vadose zone modeling of waste sites that represent a subset of the surface soil type and vegetation cover range applicable to the larger area groundwater model. The values used for the vadose zone models used to develop SSL and PRG values are within the range of recharge rates represented in the groundwater model for present day conditions.
- d. Other scenarios for future pump-and-treat operations are evaluated in the FS (Chapters 8 and 9).
- e. Specific yield is a calibration value (Section 5.6.2 of SGW-46279, Appendix F). Model input values for river stage and hydraulic properties were based on all available measurements. This parameter is a highly sensitive calibration factor in this model. Sensitivity studies would therefore necessitate recalibration for each sensitivity case.
- f. Specific storage is a calibrated value that is different from the few available values cited for other studies, but this value is unlikely to play a significant role in this application because of the shallow saturated thickness of this unconfined aquifer.

Predictive simulations were based on transient-state (that is, time-varying) conditions in the aquifer that reflect water level changes because of river stage variation. The modeling period is a 77-year period in which the first two years (2011 through 2012) are evaluated with current pump-and-treat systems operating, followed by a 75-year simulation period (2013 through 2087) without pump-and-treat operations; this represents the "no further action" condition. To allow for a balance between efficient model computer run time and resolution of river stage effects on the model predictions in the most critical early part of the simulation timeframe when the plumes are most spatially expansive and most sensitive to river stage changes. For the first 27 years (calendar years 2011 through 2037, when higher temporal resolution is needed), the modeling period consists of a series of 12 monthly stress periods that are repeated in the same sequence. These stress periods correspond to monthly average river stages, each representing the average river stage for the particular calendar month over the period 2006 to 2010, excluding 2007 values, when the river stage variation pattern was inconsistent to the other years. Exclusion of 2007 data was a decision made in model development based on review of monthly-average river stage plots for each river gauge for 2006 to 2010. In this review, it was observed that inclusion of the 2007 data, which displayed a notably different hydrograph from the other years, would have resulted in average high-river stage conditions appearing earlier in the year compared to the pattern shown in 2006, 2008, 2009, or 2010. A decision was made to base future predictions on average conditions for these 4 years that exhibited a comparable pattern. It is assumed that these conditions are representative of the typical conditions in the field and that future conditions will not vary significantly from these conditions. For the remaining 50-year period (2038 through 2087, when less temporal resolution is required because the contaminant mass remaining is not as near to the river and is consequently less sensitive to the river stage variation pattern), a single stress period is used, with the river stage elevation remaining constant, reflecting annual average conditions corresponding to 2006 to 2010 average elevations for the month of January, which was the month selected as most approximating the annual average of monthly average river stages. This approach allows for generation of a substantial body of simulation information to evaluate the apparent effects of seasonal river stage transients on transport, but also provides for efficient long-term transport estimate and plume behavior calculations.

Modeling results will support system performance evaluation considering attainment of river protection and aquifer cleanup levels (SSLs or PRGs). For this purpose, an estimate of hydraulic containment in 2012 and plume depictions at selected intervals are developed and discussed in the following text.

## 5.8.3.1 Hydraulic Containment in 2012

Based on the groundwater modeling results, a systematic approach was developed and applied to the estimated hydraulic containment in 2012. Although a single depiction of capture can be calculated using particle tracking when a model simulates quasi-steady-state conditions, an estimate of the approximate extent of hydraulic capture was calculated with the transient model. The approach was similar to that described in "The Capture Efficiency Map: The Capture Zone Under Time-Varying Flow" (Festger and Walter, 2002) and "Sources of Water to Wells for Transient Cyclic Systems" (Reilly and Pollock, 1996), focusing on the evaluation of the temporal variation in capture because of changing flow patterns and hydraulic gradients:

- Releasing particles near the end of each of the 12 monthly stress periods and simulating their migration using a very low effective porosity, ensuring that particle travel times are essentially instantaneous
- Recording the instantaneous fate of each particle during each stress period
- Calculating a capture zone for each stress period based on the "snapshot" of aquifer conditions at the time of the particle release; in this case, producing 12 instantaneous snapshots of the extent of capture
- Constructing a capture efficiency map by counting the number of times a particle originating from a location was captured by a well, and dividing this count by the total number of releases (that is, 12)

Figure 5-14 shows the current capture efficiency of the 100-DX/HX pump-and-treat system for the unconfined aquifer underlying 100-D/H. The calculated capture efficiency suggests there are areas where the capture is very efficient and areas where the capture is less efficient, although always above 50 percent. Areas of efficient capture encompass almost the entire Cr(VI) plume footprint providing river protection by achieving the state water quality standard (WAC 173-201A, "Water Quality Standards for Surface Waters of the State of Washington") ( $10~\mu g/L$ ) in the groundwater along much of the shoreline, particularly close to the pump-and-treat wells. Areas where capture is less efficient include only parts of the plume footprint near the shoreline, where pump-and-treat wells are absent or relatively sparsely placed. The ability to place wells close to the shoreline is constrained by cultural resource issues, ecological resource issues, and topographical limitations because of the steep riverbank in many locations.

This evaluation considered a "no further action" condition, with pump-and-treat operations simulated as ending after 2012, as the baseline. The continued operation of the current pump-and-treat system past 2012, as well as selected optimization schemes for extraction and injection well placement and operation for continued pump-and-treat system operations are evaluated as alternatives in the FS (presented in Chapter 8 and 9).

## 5.8.3.2 Contaminant Plume Migration

To present a simulated baseline of groundwater contaminant migration at 100-HR-3 OU, the results of simulations described as Alternative 1, which does not include continued active pump-and-treat groundwater remediation in future years (no further action after December 2012), are shown in the following figures:

- Figures 5-15 to 5-20 show the simulated dissolved Cr(VI) plume distribution in December in the years 2012, 2015, 2020, 2040, 2060, 2070, and 2087, respectively, based on the current well configuration and treatment system. (Note: Figure 5-11 showed the initial condition for dissolved Cr(VI) plume at start of January 1, 2011 based on initial conditions developed from groundwater plumes reported for calendar year 2011.)
- Figures 5-21 to 5-30 show the simulated plume distributions for strontium-90 in December in the years 2012, 2015, 2020, 2030, 2040, 2050, 2060, 2070, and 2087, respectively. (Note: Figure 5-12 showed the initial condition for dissolved strontium-90 plume at start of January 1, 2011 based on initial conditions developed from groundwater plumes reported for calendar year 2011.)
- Figures 5-31 to 5-38 show the simulated plume distributions for nitrate in December in the years 2012, 2015, 2020, 2030, 2040, 2060, 2070, and 2075, respectively. (Note: Figure 5-13 showed the initial condition for dissolved nitrate plume at start of January 1, 2011 based on initial conditions developed from groundwater plumes reported for calendar year 2011.)

The depicted plumes were simulated assuming the current pump-and-treat system is turned off on December 31, 2012. Each model simulation is run either until the modeling period expires or the COC is below the respective AWOC or MCL.

Plume migration patterns under Alternative 1 conditions (with no active pump-and-treat operations after December 2012) indicate that all of the mobile contaminants migrate (typically across the Horn) toward, and ultimately discharge into the Columbia River. The predicted concentrations of the contaminants decrease according to their natural decay rate (for example, for radionuclides), or because of dispersion as they move through the aquifer. Those contaminants with low attenuation (that is, low  $K_d$ ) move more rapidly toward the river than those with higher attenuation (that is, higher  $K_d$ ).

Prediction results for Cr(VI) in groundwater underlying 100-D/H show that the highest concentrations of Cr(VI) persist along the shoreline of 100-D (Figure 5-21). The shoreline is where initial concentrations above 40,000  $\mu$ g/L attenuate slowly and stay above the 10  $\mu$ g/L level for more than 75 years under natural fate and transport conditions (if the pump-and-treat system is turned off at the end of CY 2012). The highest concentrations remain between the 100 and 500  $\mu$ g/L concentration contour interval. Therefore, the model simulation predicts that after 75 years of natural attenuation Cr(VI) concentrations in groundwater would exceed the AWQC value of 10  $\mu$ g/L at points where groundwater discharges to surface water.

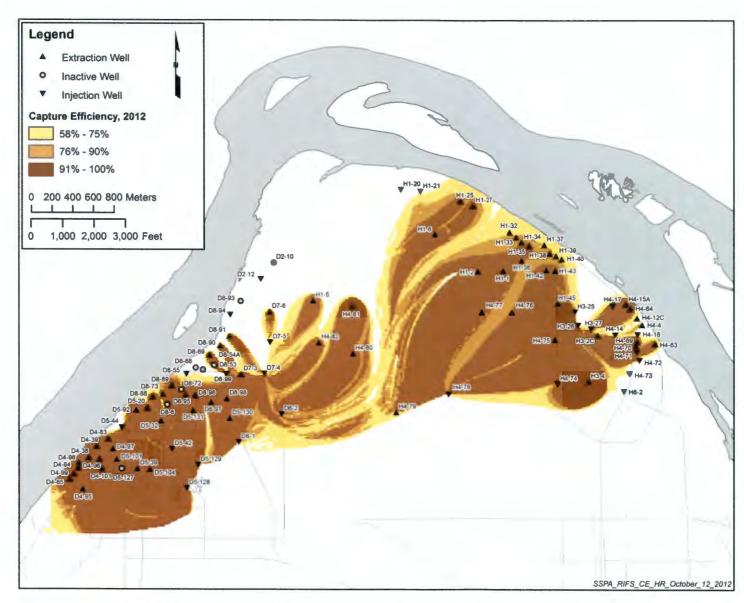


Figure 5-14. Approximate Extent of Capture throughout 100-D/H for January to December 2012

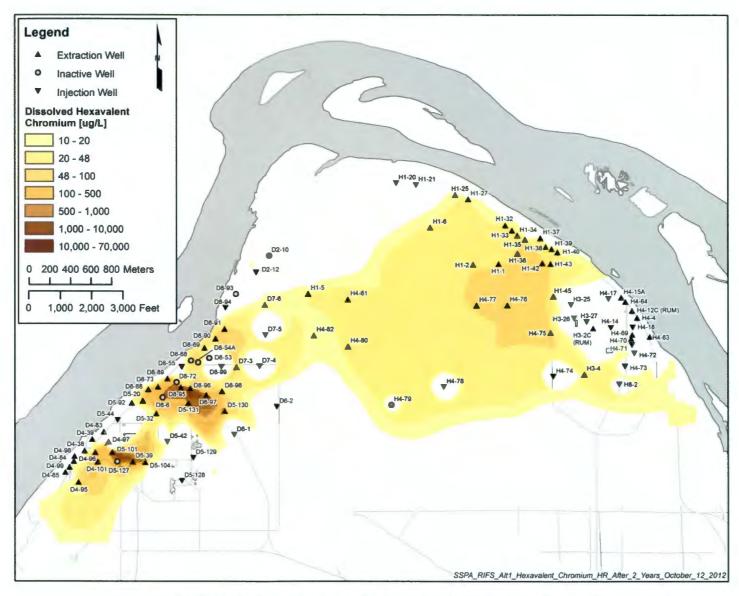


Figure 5-15. Model-Simulated Dissolved Cr(VI) Distribution after 2 Years (Based on No Further Action)

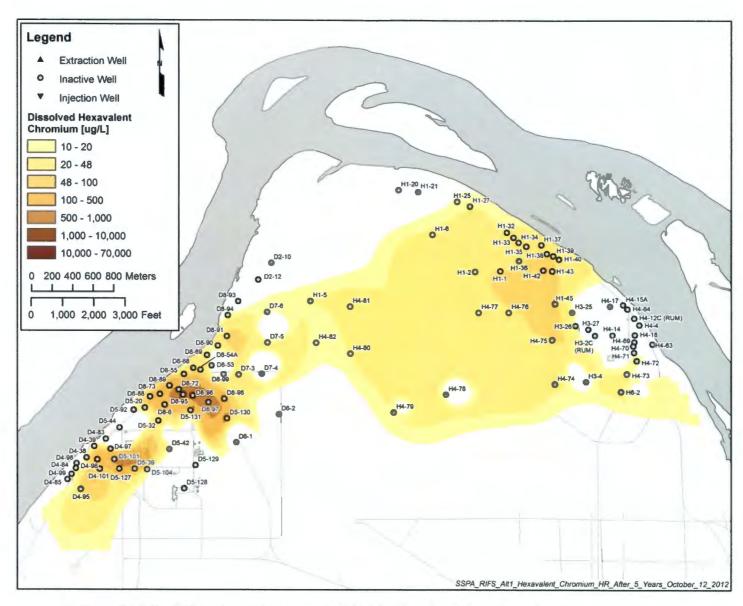


Figure 5-16. Model-Simulated Dissolved Cr(VI) Distribution after 5 Years (Based on No Further Action)

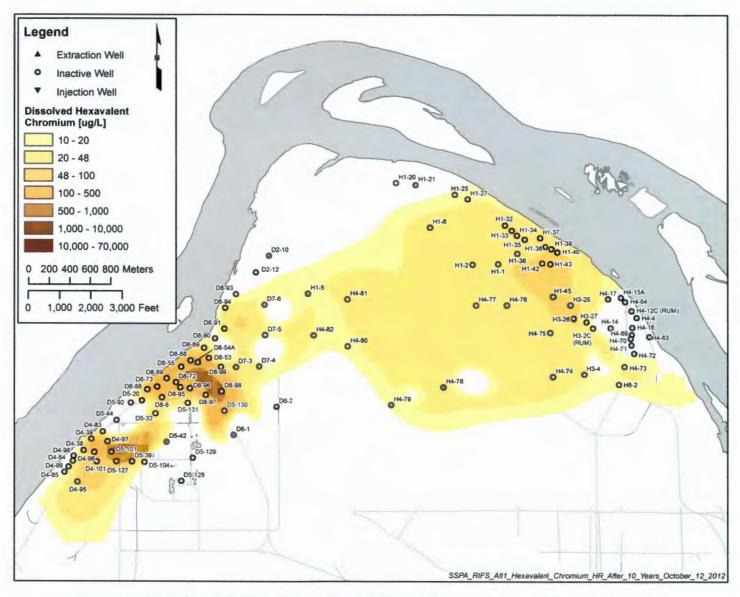


Figure 5-17. Model-Simulated Dissolved Cr(VI) Distribution after 10 Years (Based on No Further Action)

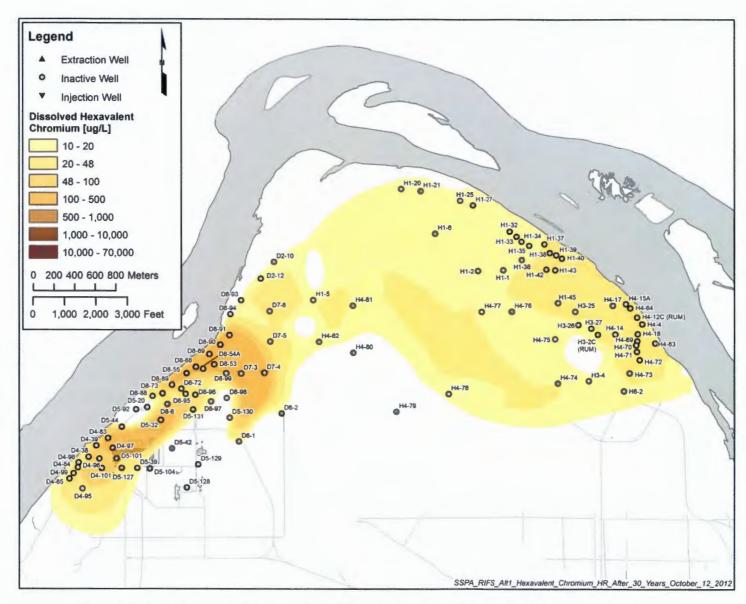


Figure 5-18. Model-Simulated Dissolved Cr(VI) Distribution after 30 Years (Based on No Further Action)

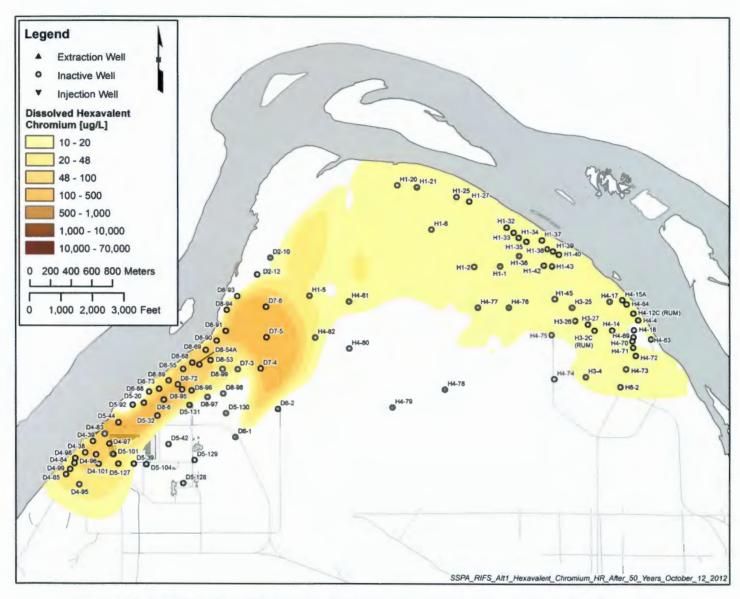


Figure 5-19. Model-Simulated Dissolved Cr(VI) Distribution after 50 Years (Based on No Further Action)

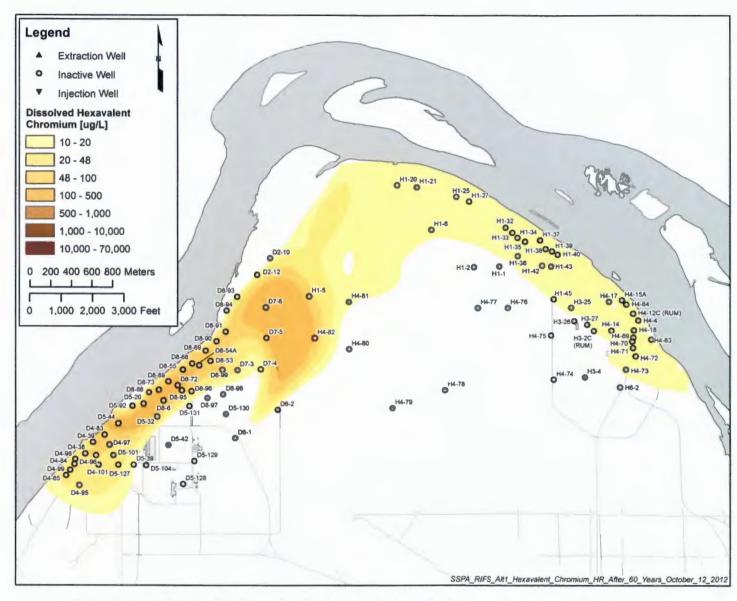


Figure 5-20. Model-Simulated Dissolved Cr(VI) Distribution after 60 Years (Based on No Further Action)

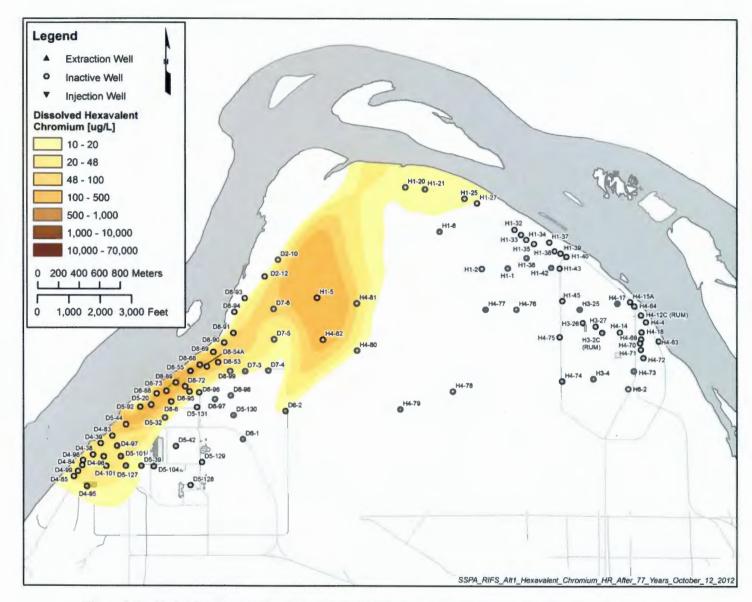


Figure 5-21. Model-Simulated Dissolved Cr(VI) Distribution after 77 Years (Based on No Further Action)

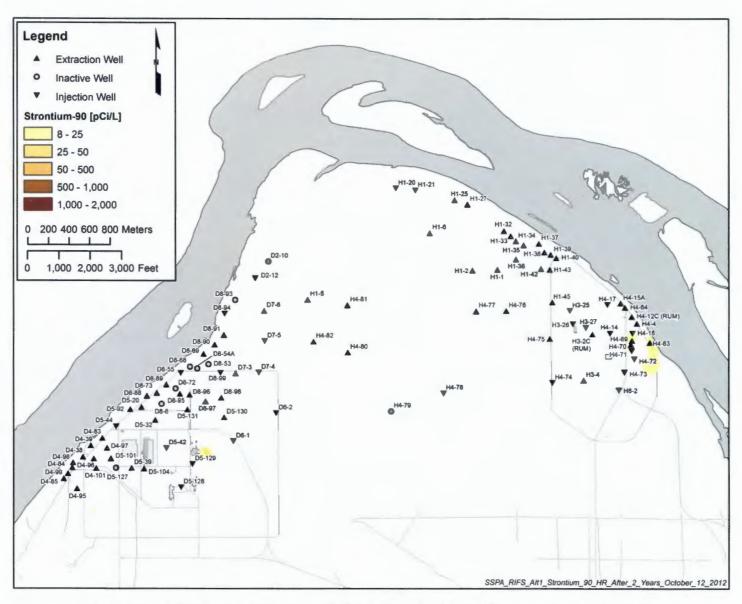


Figure 5-22. Model-Simulated Strontium-90 Distribution after 2 Years (Based on No Further Action)

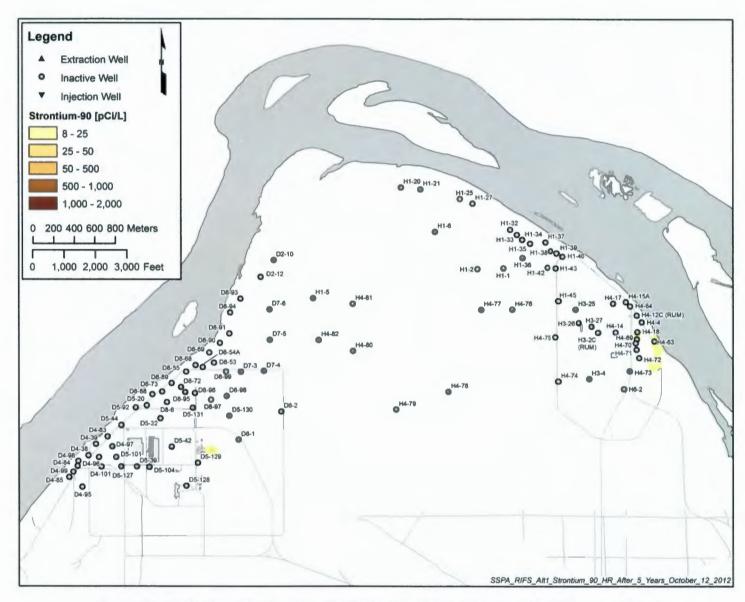


Figure 5-23. Model-Simulated Strontium-90 Distribution after 5 Years (Based on No Further Action)

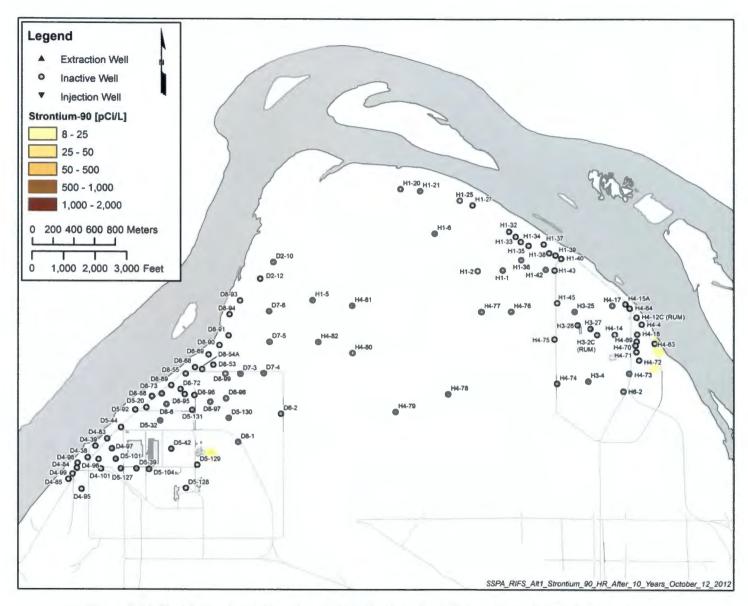


Figure 5-24. Model-Simulated Strontium-90 Distribution after 10 Years (Based on No Further Action)

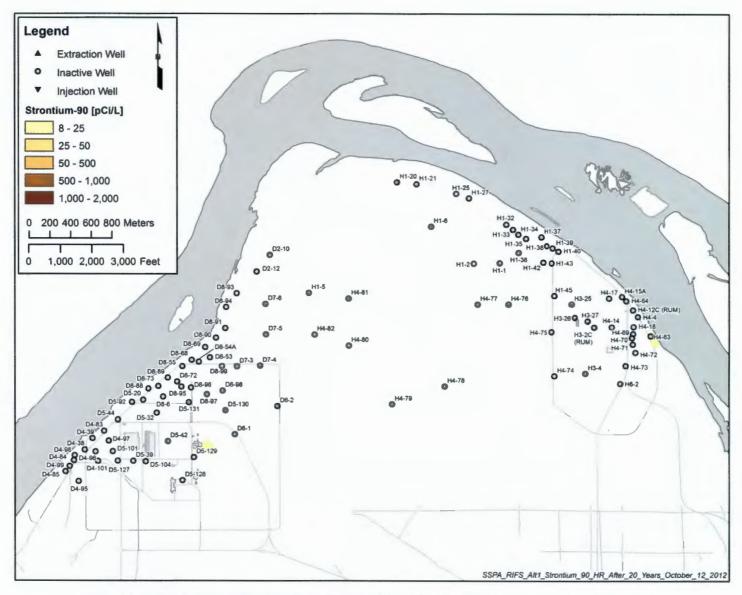


Figure 5-25. Model-Simulated Strontium-90 Distribution after 20 Years (Based on No Further Action)

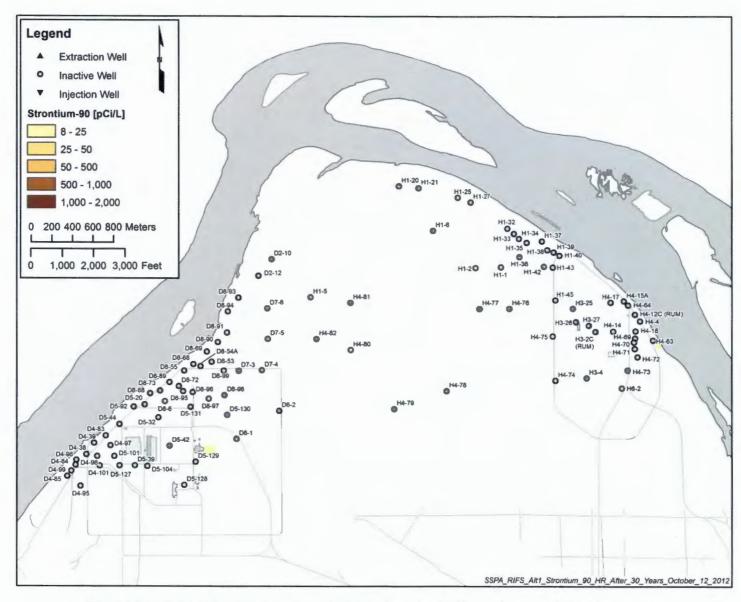


Figure 5-26. Model-Simulated Strontium-90 Distribution after 30 Years (Based on No Further Action)

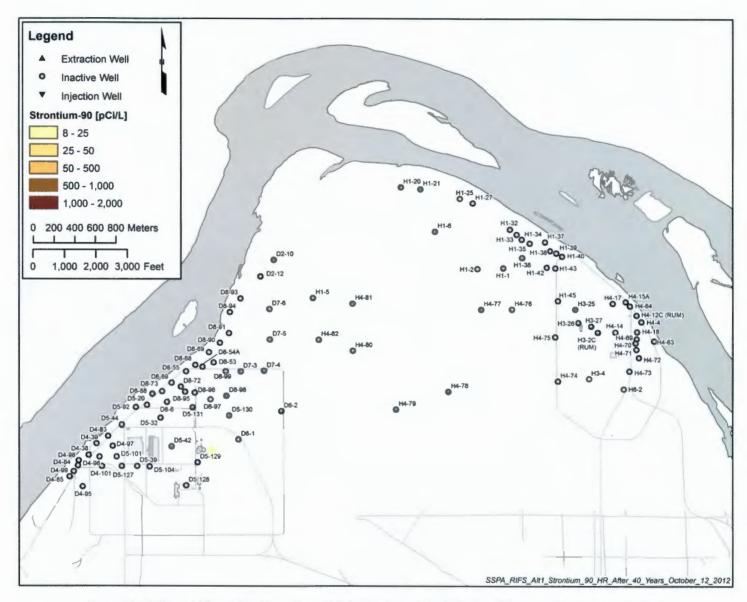


Figure 5-27. Model-Simulated Strontium-90 Distribution after 40 Years (Based on No Further Action)

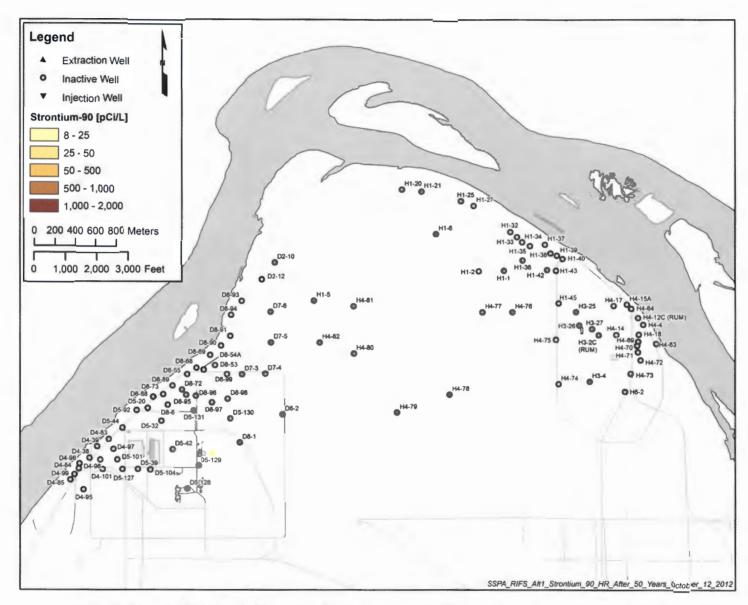


Figure 5-28. Model-Simulated Strontium-90 Distribution after 50 Years (Based on No Further Action)

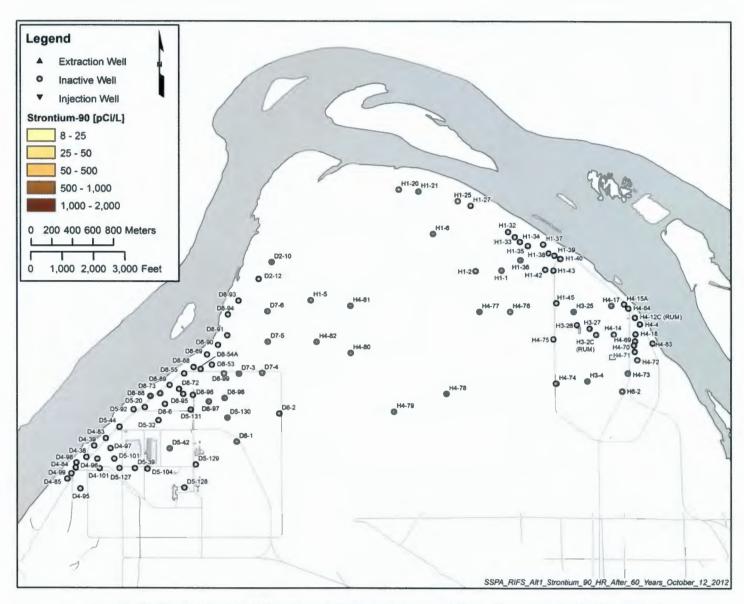


Figure 5-29. Model-Simulated Strontium-90 Distribution after 60 Years (Based on No Further Action)

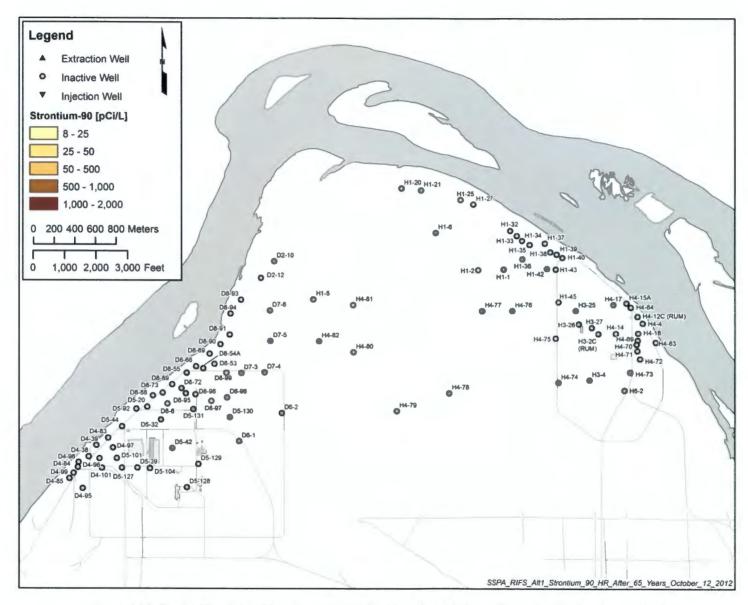
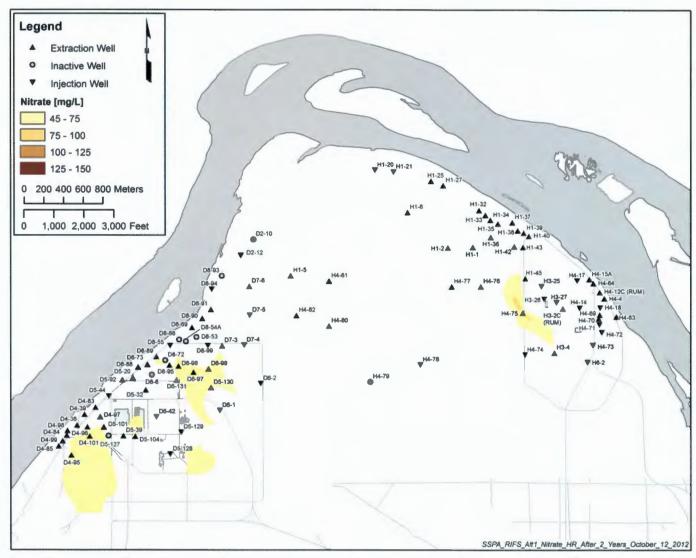


Figure 5-30. Model-Simulated Strontium-90 Distribution after 65 Years (Based on No Further Action)



Note: The elevated nitrate concentration areas evident near Wells H4-75 was based on the source used for development of the initial condition for nitrate, but that plume depiction was subsequently investigated and determined to be based on erroneous data; a revised depiction of current nitrate conditions is provided in Figure 4-90. Modeling was not repeated for nitrate to correct for this nitrate plume because predictive simulations did not indicate the fate of this non-existent plumes would lead to a need for action (note the attenuation shown in the subsequent nitrate figures.

Figure 5-31. Model-Simulated Nitrate Distribution after 2 Years (Based on No Further Action)

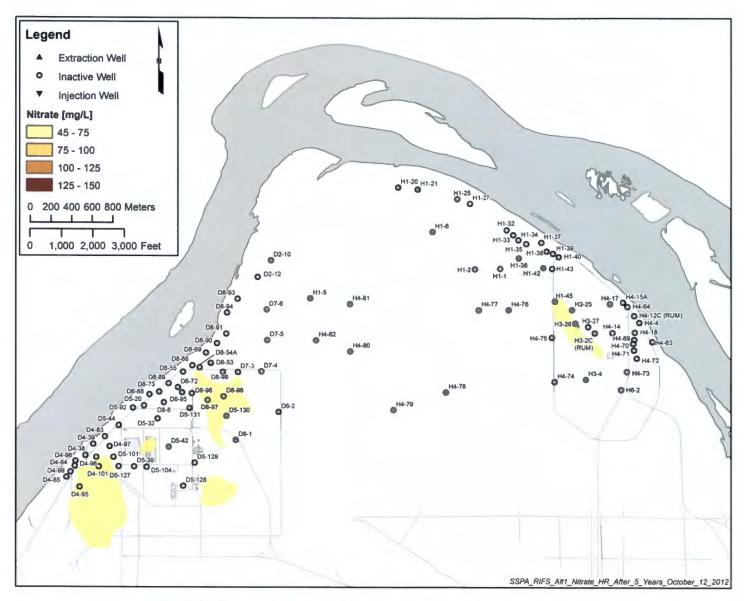


Figure 5-32. Model-Simulated Nitrate Distribution after 5 Years (Based on No Further Action)

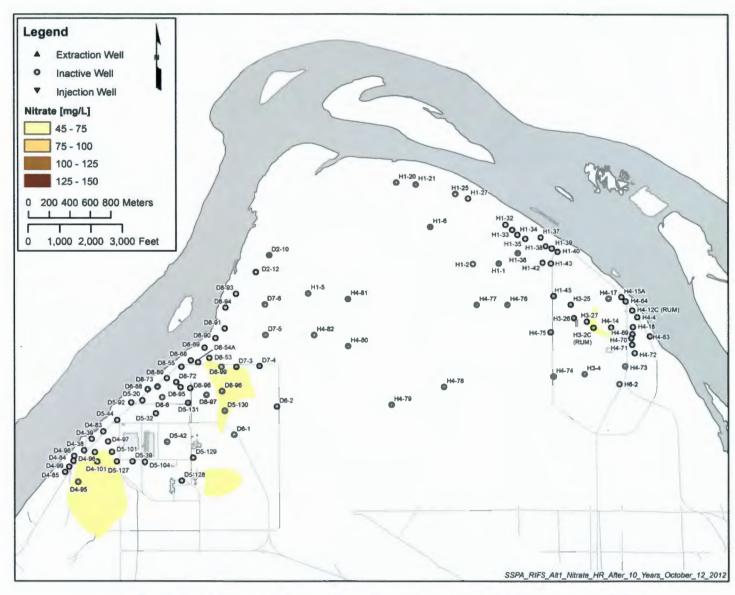


Figure 5-33. Model-Simulated Nitrate Distribution after 10 Years (Based on No Further Action)

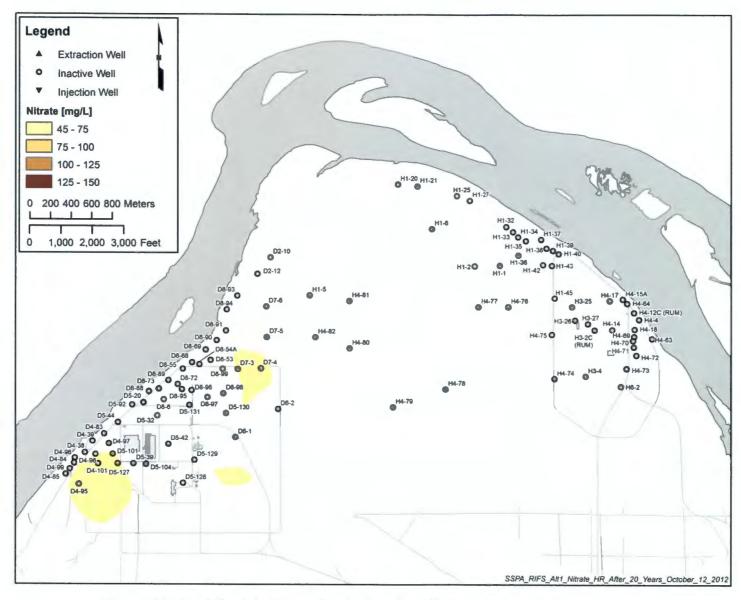


Figure 5-34. Model-Simulated Nitrate Distribution after 20 Years (Based on No Further Action)

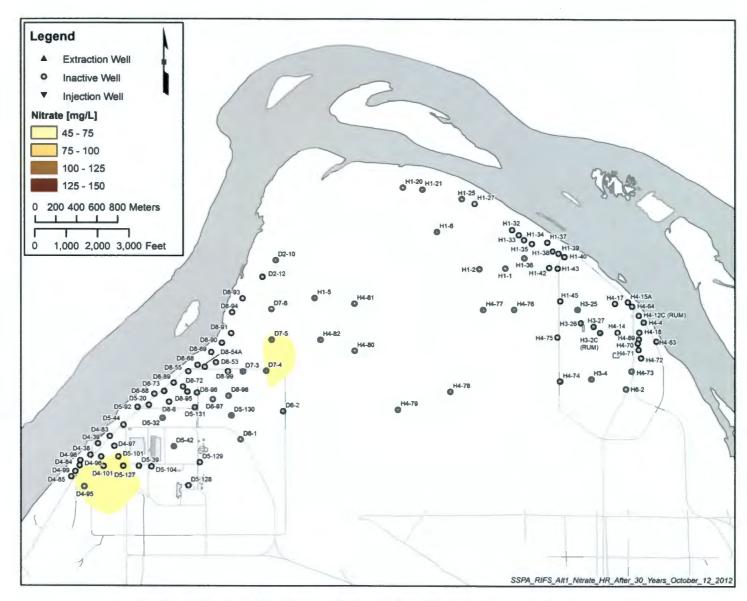


Figure 5-35. Model-Simulated Nitrate Distribution after 30 Years (Based on No Further Action)

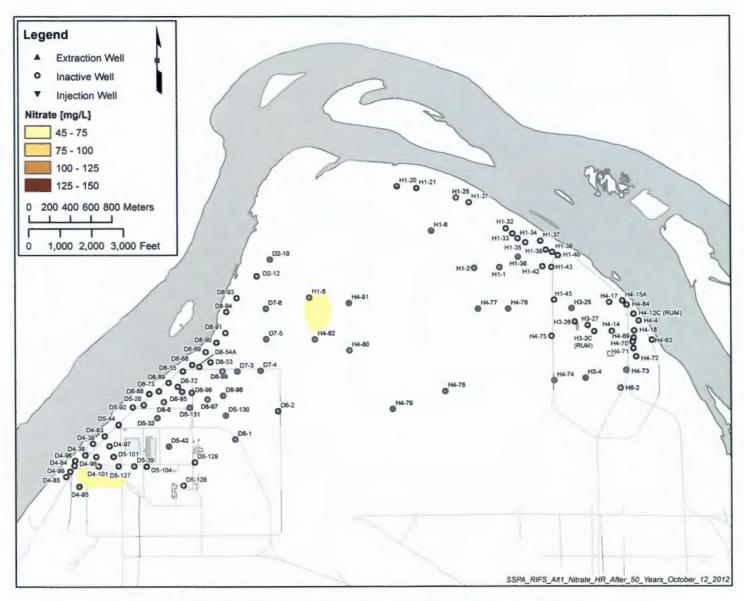


Figure 5-36. Model-Simulated Nitrate Distribution after 50 Years (Based on No Further Action)

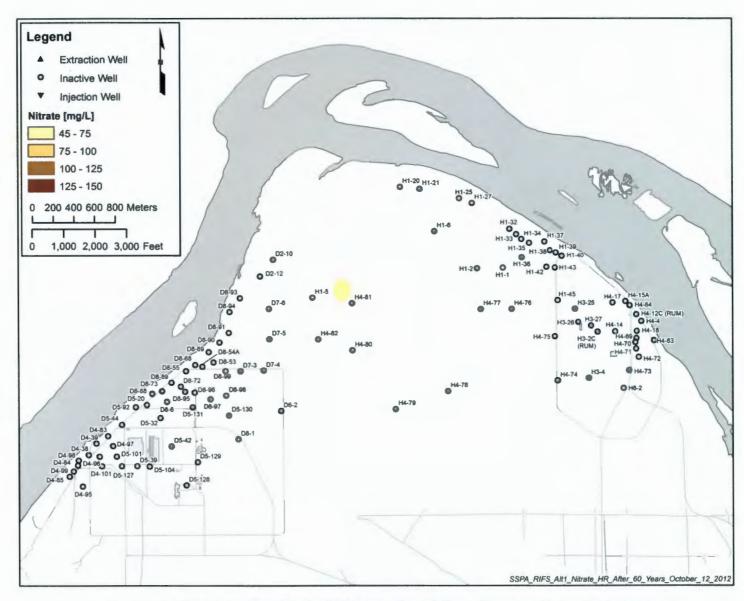


Figure 5-37. Model-Simulated Nitrate Distribution after 60 Years (Based on No Further Action)

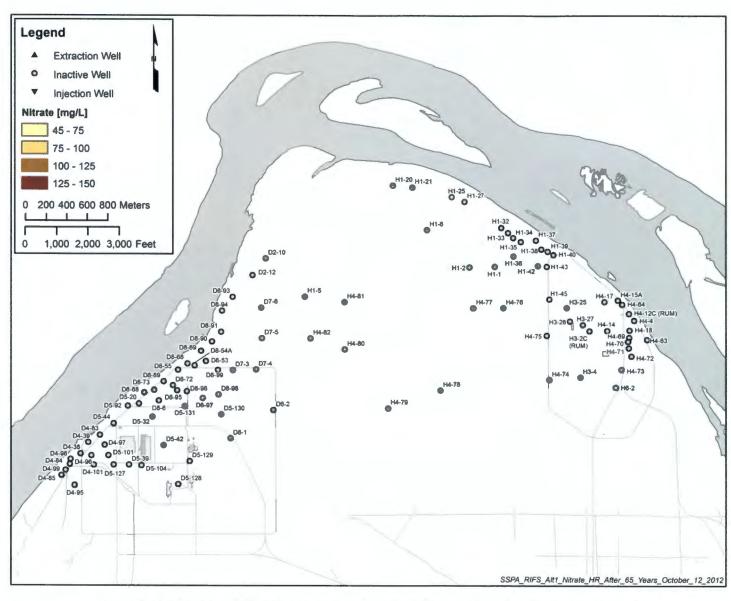


Figure 5-38. Model-Simulated Nitrate Distribution after 65 Years (Based on No Further Action)

When groundwater pump-and-treat remedial systems are initially developed and evaluated in an FS, a two-tiered approach to defining the system components (number of wells, well locations, and flow rates) is used. This two-tiered approach includes simulating the performance of a remedial systems (that is, mass removal and time to cleanup) using the COCs maximum concentration over times, as well as using the COCs EPC value over time. The maximum concentration simulations provide the most conservative analysis of the systems performance and the EPC simulation provides reasonably expected results (with a statistical confidence level of 95 percent). From these simulations, the systems components are identified, including a range from short times to cleanup using aggressive mass removal approaches to longer periods that remove less mass and take advantage of various degrees of natural attenuation. The remedial alternatives resulting from these simulations (using the maximum and the EPC approach) cover a broad range of performance, times to cleanup, certainty in achieving the predicted performance and overall remedy life-cycle cost. Remedy system performance data and groundwater compliance demonstration data that show cleanup levels have been met will be generated using guidance provided by Washington State ("Groundwater Cleanup Standards" [WAC 173-340-720(9)(d)(i)]) and EPA (Methods for Evaluating The Attainment Of Cleanup Standards Volume 2: Ground Water [EPA 230-R-92-014]). These guidance documents support the use of a broad and robust monitoring well network and the use of a statistical data presentation such as an EPC. Therefore, the remedial alternatives performance criteria are generally defined using the statistical EPC approach, while understanding the implications of the COC maximum concentrations and where in the OU those maximum concentrations occur for the longest time (e.g., hot spots and isolated areas above cleanup levels). The monitoring well network and performance monitoring program will be defined in the remedial design phase of the project. This monitoring is an important tool in future process optimizations. The groundwater transport model is used to present the predicted efficacy of alternative pump-and-treat strategies in the FS.

## 5.9 Uncertainties that Apply to Groundwater and Vadose Zone Modeling

This uncertainty discussion is based primarily on the current vadose zone and groundwater modeling objectives, and the use of these models to evaluate future conditions under no action and active remediation scenarios. Although these uncertainties exist and must be considered in decision making, conservative assumptions incorporated into the vadose zone and groundwater transport simulations can reduce the effects of uncertainty on successfully remediating 100-D/H waste sites and groundwater.

## 5.9.1 Uncertainty in the Conceptual Site Model

Conceptual model uncertainty is often the main uncertainty when using models to predict future contaminant fate and transport. Assumed values for vadose zone and aquifer physical properties, together with assumed values for contaminant transport properties, contribute to overall predictive uncertainty. Assumptions of spatially invariant material properties are often necessary to develop initial flow and transport models to perform and obtain acceptable calibration, despite the recognition that the processes that deposited the soil materials produce stratified and heterogeneous sequences. Local variation in vadose and/or aquifer material properties can result in contaminant transport variations. Conceptual model uncertainty is discussed below for both vadose zone transport modeling and for groundwater transport simulations.

The assumption of constant effective porosity and saturated hydraulic conductivity values for a given stratigraphic unit is made in calculating screening levels and PRGs protective of groundwater and surface water, as well as in converting the Darcy flux (as calculated by MODFLOW) to average linear groundwater velocity (as used in MODPATH and MT3DMS) for fate and transport calculations. In addition, the heterogeneity in the form of discontinuous structures (lenses), bar structures, and overbank deposits that is common at a scale below the grid size of the 100-D/H groundwater models is

not accounted for in the Tier 1 screening level calculations or the Tier 2 STOMP 1D PRG model calculations. Some of these features can lead to locally faster contaminant movement than predicted by models that assume spatially invariant properties, although over broad areas, the average values for predictions will be similar whether small-scale heterogeneity is—or is not—represented. The effects of these local-scale uncertainties on predictions of groundwater and surface water protection metrics are minimized to the practical extent possible by building in conservatism using the lowest screening level and calculated PRG resulting from the STOMP simulations.

Perhaps one of the largest uncertainties in the CSM for groundwater simulations at 100-D/H is the potential for continued contribution of contaminants to groundwater from residual vadose zone sources. The groundwater contamination transport simulations discussed previously do not include the effects of any continuing releases to groundwater (that is, they assess the behavior of existing groundwater contaminant plumes only). The potential for continued release of contaminants from contaminated vadose zone soil remains uncertain. After cessation of reactor operations and cooling water treatment and disposal activities at 100-D/H, the driving force of artificial water discharge to the soil for downward movement of mobile contaminant has been largely eliminated. For example, the south groundwater Cr(VI) plume underlying 100-D has exhibited persistent elevated concentrations. This is likely the result of some degree of continuing contribution from the vadose zone. Section 4.3.20 describes known vadose zone waste sites with Cr(VI) soil-contamination at various stages of active remove, treat, and dispose remediation under interim action decisions. The nature of this potential contribution is also uncertain. There are localized regions within the vadose zone that contain measureable quantities of mobile contaminants. Potentially, contributions to groundwater contamination may occur from natural or artificial recharge water (for example, dust-control water) moving downward through the vadose zone and carrying mobile contaminants to groundwater. Historical groundwater monitoring data indicate that in some locations (for example, Wells 199-D5-99 and 199-D5-122), groundwater Cr(VI) concentrations exhibit increasing concentration transient trends apparently associated with periods of anthropogenic increases in groundwater elevation. This suggests the possibility that groundwater entering portions of the deep vadose zone at those locations at elevations above the normal natural seasonal fluctuation range may mobilize residual soil contaminants. Similar uncertainty may also exist at other areas of historical releases to the ground. Following the ROD, the groundwater monitoring program will be reviewed and revised if necessary to address the goals of the ROD. The RPO process will be used to provide ongoing evaluations to ensure the system meets ROD performance requirements (Chapter 9).

#### 5.9.2 Uncertainty in the Initial Contaminant Distribution

Uncertainties with estimating contaminant distribution are primarily associated with the interpolation of individual sample contaminant concentration and the representativeness of individual samples with respect to the region surrounding the sample. The sample contaminant concentration is a minor contributor to overall uncertainty because of stringent quality controls applied by analytical laboratories. However, the representativeness in time and space of samples, together with the uncertainty associated with the interpolation of those point sample values to make a continuous distribution, is likely the greatest contributor to overall uncertainty in the initial contaminant distribution for both vadose zone and groundwater simulations.

The distribution of groundwater contaminants across the entire thickness of the saturated model domain for groundwater simulations is presented at a bounding representation of the contaminant conditions. Investigative approaches such as collection of groundwater grab samples during well drilling help reduce this uncertainty by providing information on vertical contaminant distribution in groundwater.

Evaluation of the vertical distribution of contaminants across the full thickness of the vadose zone for the SSL and PRG simulations for low  $K_d$  contaminants and upper 70 percent of vadose zone for high  $K_d$ 

contaminants is believed to be representative (with conservative bias) based on observations of actual contaminant distribution made during the RI. However, data from the RI boreholes revealed cases where it was suspected this 70:30 profile might be non-conservative. A process was followed to identify cases that needed further evaluation. The conservatism in the identified cases was tested by comparing simulations of actual contamination profiles with the 70:30 profile to determine which yielded higher peak groundwater concentration predictions. The results of this testing demonstrated the 70:30 profile was conservative (that is, resulted in more restrictive SSL and PRG values than would be obtained using available profile data) for all cases evaluated. This was the case because simulating actual borehole concentration profiles yielded lower peak groundwater concentrations than for the 70:30 profile. This evaluation is described in Section 5.7.2. Had this evaluation revealed non-conservative cases, then under the graded approach to vadose zone modeling in which sites with observed conditions not well represented by the default SSL and PRG simulation conditions would have been reconsidered with site-specific modeling as described in Section 5.1, and presented on Figure 5-1. However, in 100-D/H no such cases occurred and site-specific modeling was not necessary.

An exception to the assignment of initial source distributions based on  $K_d$  is made in the case of strontium-90, owing to the observed distribution of this COPC at depths greater than the upper 70 percent of the profile for this COPC in numerous locations. This distribution is a legacy of the greater mobility of this contaminant in the operational era under different geochemical and hydraulic conditions than are prevalent in the present or anticipated in the future. Accordingly, despite a  $K_d$  value higher than the 2 mL/g threshold, the 100:0 profile is applied for evaluation of strontium-90.

The default SSL and PRG simulation calculations assumed that the contaminants are distributed uniformly over the vadose zone thickness (full thickness for low  $K_d$  contaminants and strontium-90, upper 70 percent of the thickness for all other high  $K_d$  contaminants) beneath the remediated waste site. If contaminants are actually limited to the near-surface portion of the vadose zone (a non-conservative condition relative to the assumed uniform contamination profile), then the SSL and PRG simulations will lead to an overly conservative assessment of the potential threat to groundwater or surface water. For example, if a contaminant is only distributed over the uppermost 10 percent of the soil profile, then representing it with the bounding initial uniform contaminant distribution at the level measured near the surface (either the 100:0 or 70:30 model) will result in an earlier peak groundwater concentration, because this contamination would be represented lower in the soil profile than it actually occurs. Further, in this example, the peak groundwater concentration would be higher because less attenuation would occur where the contaminant mass is initially lower in the profile. The higher peak groundwater concentration resulting from the bounding representation of initial contaminant distribution (100:0 or 70:30 model) in the soil profile then would result in more restrictive SSL and PRG values in this example because these are a function of the calculated peak groundwater concentration.

The majority of the residual contamination is expected to occur in the fine-grained (<2 mm size) portion of the sediments in the vadose zone. However, considerable uncertainty exists in the spatial variation in fraction of fine-grained material within the vadose zone. For modeling, the residual contaminant concentration determined in the laboratory on the fine-grained sediments is applied to the bulk volume, thereby increasing the initial mass estimate. This overestimation of initial mass, in turn, leads to overestimation of peak groundwater contamination in the vadose zone transport modeling, resulting in low (more restrictive) SSL and PRG values compared to what would be calculated with a more realistic treatment of the bulk volume.

Additional uncertainty with respect to initial contaminant concentrations is introduced by measurement of contaminants at concentrations that exceed the 90<sup>th</sup> percentile background concentration but are less than the maximum of the background concentration range. This condition is observed at several sites in

100-D/H where arsenic EPCs exceed the 90<sup>th</sup> percentile concentration, but are less than the maximum reported background concentration (*Soil Background for Interim Use at the Hanford Site* [ECF-HANFORD-11-0038] in Appendix D). The initial contaminant concentration rules applied in general vadose zone modeling (100:0 and 70:30 profiles) function as a bounding condition with respect to the predicted peak groundwater concentration, so the impact of not using these measurements would have only a small likelihood of results in a less bounding initial condition.

### 5.9.3 Uncertainty in Contaminant Transport Parameters

Parameters that affect contaminant transport include the particle density, dispersion coefficients, radiological half-life for each radiological contaminant, the  $K_d$  for each contaminant, and soil porosity. There is relatively little uncertainty (but limited variability) in the mean values for particle density. There no significant uncertainty or variability (for purposes of groundwater modeling) in the values for radiological half-lives.

Hydrodynamic dispersion was conservatively assumed negligible, so dispersivity values were all set to zero in vadose zone modeling. Setting dispersivity values to zero yields higher peak groundwater concentrations than would be obtained using non-zero values. This, therefore, is a bounding assumption with respect to SSL and PRG values. Numerical dispersion is a separate consideration; steps taken to minimize numerical dispersion in the STOMP code calculations are discussed in Appendix F, ECF-Hanford-11-0063, Section 3.1.) For the saturated zone modeling, macrodispersivity is a scale-dependent parameter and can only be determined from inverse modeling of tracer tests on the scale of interest. Because very few such large-scale tracer tests have been conducted, and none has been conducted at the Hanford Site, the macrodispersivity values used in the groundwater transport model were not based on Hanford Site data. However, longitudinal macrodispersivity for the Hanford formation and Cold Creek gravel unit is considered to generally lie within the range of 60 to 120 m (197 to 394 ft) for a sand and gravel aquifer, as determined in "Field Study of a Long and Very Narrow Contaminant Plume" (van der Kamp et al., 1994). The recommended values for longitudinal dispersivity and transverse dispersivity for use for groundwater transport modeling were developed in Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model (SGW-46279) in Appendix F. However, these values were recommendations only. For purposes of saturated zone modeling, the macrodispersivity values, if used, should vary with the scale of the simulation as well as to ensure that the values satisfied the grid Peclet number and Courant number constraints. In this cases, no dispersion was included (hydrodynamic dispersion was treated as negligible in the saturated zone). Actual hydrodynamic dispersion would lead to greater dispersion of groundwater plumes than predicted in the model, but also lower peak concentrations, which was the metric used to evaluate remedial timeframes.

The  $K_d$  value of a contaminant for a soil type represents the degree of partitioning of the contaminant to the surface of the soil particles compared to the dissolved concentration. These  $K_d$  values were selected for the specific purpose of calculating SSL and PRG values, and not for determination of residual contamination in the vadose zone for other pathways. Further, for Cr(VI)  $K_d$  is treated differently for Cr(VI) in the vadose zone, where the value represents the residual portion remaining in the soil column, than in the saturated zone, where sorption is simulated using a dual-porosity formulation. A high  $K_d$  value is typically found in contaminants such as aroclors (PCBs), which are generally considered hydrophobic. The lower the  $K_d$ , the more likely it is that the contaminant will move with water through the vadose zone. A  $K_d$  value can vary based on the water quality and chemistry (such as pH), the concentration of the contaminant, the type of sorbent, and the availability of sorption sites within the soil matrix. The  $K_d$  values used in evaluating the transport were primarily based on the assumption of dilute concentrations of contaminants in moisture within the vadose zone. These values tend to represent the more mobile  $K_d$  conditions for a particular contaminant, and therefore are considered bounding (conservative relative to

prediction of contaminant arrival at a downgradient location).  $K_d$  values were selected following the process noted in Appendix F, ECF-Hanford-12-0023, with precedence given to using CLARC table values if available for a given contaminant. The influence of  $K_d$  variability on peak groundwater concentration predictions in the vadose zone modeling was evaluated in a sensitivity analysis for a 100-D representative stratigraphic column in Appendix F, ECF-Hanford-12-0023, Section 6.2.1 for the irrigation recharge scenario. This sensitivity analysis showed that, for the irrigation recharge scenario, the peak groundwater concentration occurred within 1000 years of remedial action for a range of  $K_d$  values from 0.0 mL/g to 8.0 mL/g, but the magnitude and duration of the peak concentration varied with  $K_d$ . Additional sensitivity can be inferred through comparison of SSL and PRG values to  $K_d$  for the range of  $K_d$  values simulated for different COPCs; it is for this reason that the SSL and PRG values are provided in ascending  $K_d$ -order in the tabulated results in Attachments A and B to ECF-Hanford-11-0063 (Appendix F).

Soil porosity is variable throughout the soil column based on compaction and soil type heterogeneity. As soil porosity increases, so does the contaminant mass flux to the water table; accordingly, the uncertainty in actual formation porosity will be reflected in uncertainty in the contaminant mass flux. A best estimate of the porosity is used in constructing the model. However, it is acknowledged that there is uncertainty in these estimates. The Vadose Zone Hydrogeology Package (PNNL-14702, Appendix B) provides estimates of the uncertainty in soil hydraulic parameters, including porosity, based on variability in data used to derive these model parameters. Based on the information presented in that reference, the porosity of Hanford formation sediments can be represented as normally distributed with a standard deviation of no more than 0.10. Ringold Formation sediments are slightly more variable, where porosity can be represented as normally distributed with a standard deviation no larger than 0.14.

## 5.9.4 Uncertainties, Assumptions, and Limitations Specific to Vadose Modeling

Uncertainties based on the numerical equations used in modeling are expected to be small. *Regulatory Basis and Implementation of a Graded Approach to Evaluation of Groundwater Protection* (DOE/RL-2011-50) provides a summary evaluation of the comparisons of field data and results to the model simulations of similar conditions using STOMP. The evaluations have shown through comparison to analytical solutions, benchmarking against other simulation codes, and field validation that the STOMP code adequately solves the governing equations it incorporates for flow and transport processes correctly. However, the representativeness of any given model implemented using STOMP is inherently limited by the accuracy of the conceptual representation and the representativeness of the parameterization applied in that model. *Model Package Report: Vadose Zone Model for the River Corridor* (SGW-50776) includes a detailed evaluation of uncertainties, assumptions, and limitations to the vadose zone model used for this study.

Several conservative assumptions and parameter values are used in the vadose zone modeling to ensure the SSL and PRG values calculated with this model are deliberately biased toward bounding (more restrictive) values. These conservative assumptions and parameters apply only to modeling conducted to calculate SSL and PRG values for protection of groundwater and of surface water resources. These conservative assumptions and parameters are not applicable to the calculation of residual soil contamination for purposes of calculating direct exposure, which is a separate calculation presented in Chapter 6.

The representativeness of soil samples collected during drilling and the resultant chemical analyses of those samples are subject to some degree of uncertainty. A limited number of soil samples in some boreholes may have been affected by water added during drilling in the vadose zone. The most likely effect of this condition, if it can be confirmed to have occurred, is that the added water may have wetted the underlying soil above its natural condition, and if wetting was sufficiently great, some movement of

mobile contaminants may have occurred in soil immediately beneath the drill string at the point of water addition. The magnitude of the effect of this condition is difficult to quantify; a limited number of borehole soil samples may have been affected by water added during drilling and the resultant chemical results are subject to some degree of uncertainty. The magnitude of the effect of this condition is difficult to quantify, as discussed in Section 4.3.21. Additional uncertainties related to specific measurements (for example, batch leach tests) are discussed earlier in this chapter.

Assumptions within the model input parameters impose limitations on the model and have an effect on the simulation outcomes. The key assumptions used for 100-D/H are as follows (with other assumptions presented in STOMP 1-D Modeling for Determination of Soil Screening Levels and Preliminary Remediation Goals for Waste Sites in the 100-D and 100-H Source Operable Units [ECF-HANFORD-11-0063] in Appendix F):

- The vadose zone is considered homogeneous in nature, within the stratigraphic cross sections developed for the simulations, without consideration to the presence of thin finer grained material, which can retard the downward migration of contaminants. This constitutes a balanced representation of the vadose zone with respect to contaminant arrival time and peak groundwater concentration. If preferential pathways exist, these would function to decrease arrival time and, potentially, increase peak groundwater concentration. Such pathways are difficult to identify in most cases, but if present would be surmised to have had the largest impact prior to the present. The model is therefore limited to a one-dimensional representation of flow and transport in the vadose zone; lateral spreading cannot be simulated.
- Based on current revegetation activities, revegetation of a waste site after remediation is typically occurring within one to two growing seasons. In the modeling, revegetation of the area is assumed to start after 5 years, with bare soil present for the first 5 years. This assumption results in more water infiltrating to the vadose zone than may actually occur. This not a limitation of the model (which can simulate any number of recharge scenarios), but rather is a parameterization of a postulated future land use with direct implications for applicable recharge rate variation with time.
- The estimated recharge scenario used in development of SSLs and PRGs includes a progression from bare ground through developing shrub-steppe plant community to a long-term mature shrub-steppe community. This recharge scenario may be subject to specific uncertainty because of the potential for wildfire effects. Wildfires occur periodically (and can be characterized by a recurrence frequency), and the effects of these events would likely result in a net increase of the long-term recharge rate to groundwater underlying affected areas. This effect is due to the removal of the mature plant communities at the ground surface (effectively to bare ground) in a fire event, followed by a plant recovery succession, and culminating in the mature shrub-steppe community if the time until the next fire event allows. The magnitude of this effect on average recharge rates is not quantified, but would depend on factors such as the fire event recurrence frequency, the intensity of individual fire events, and the recovery periods for specific plant communities. A typical fire cycle would include the fire year, during which the surface is assumed to be bare ground and recharge is maximized, followed by rapid establishment of cheatgrass (Bromus tectorum) over 1 to 2 years. Subsequent re-establishment of the young shrub-steppe community follows, with eventual development of the mature shrub-steppe. A realistic treatment of the fire cycle should address uncertainty in the fire recurrence frequency. To account for this uncertainty, the recharge rates used in the vadose zone models are selected from the upper end of available rates based on about 30 years of field measurements (lysimeter studies) and long-term isotopic recharge studies that necessarily incorporate the effects of the history of all land surface changes at the measurement sites, including past wildfires. Again, this is not a limitation of the model (which can simulate any number of recharge scenarios), but rather is a

parameterization of a postulated future land use with direct implications for applicable recharge rate variation with time.

- Groundwater is assumed to have negligible mixing with the Columbia River. In calculating the values for surface water protection, the point of calculation is the upper 5 m (16 ft) of groundwater at the downgradient edge of the waste site. No attenuation or decay of contaminants is assumed between the source area and groundwater further downgradient of the waste, or at the river. This assumption results in conservative (more restrictive) SSL and PRG estimates because most waste sites are located some distance from the river, and some mixing will occur between the waste site and locations downgradient as well as in the river. Thus, the model is limited (deliberately and conservatively with respect to surface water protection) to simulating dilution only in the upper aquifer under the waste site.
- The 100:0 and 70:30 profiles (for low and high K<sub>d</sub> contaminants, respectively, except that strontium-90 was evaluated using the 100:0 profile despite its higher K<sub>d</sub> value) for SSL use an irrigation recharge scenario and assume the entire vadose zone below backfill is contaminated below clean fill for low K<sub>d</sub> contaminants, while the upper 70 percent of the vadose zone below backfill is contaminated for high K<sub>d</sub> contaminants. The initial conditions (either the 100:0 or 70:30 profile) represent bounding initial conditions that effectively assume the maximum residual soil contamination level is uniformly present over the entire applicable vadose zone thickness. This is bounding because the peak concentration in the vertical profile would not be expected to occur over the entire depth range. No waste sites were identified in the analysis for site-specific analysis, based on evaluation of the conservatism of the 70:30 profile for sites identified as potentially being unrepresentative in the RI borehole data reported in Chapter 4. The PRG development used these same initial source distributions, but with a recharge scenario based on reestablishment of natural net infiltration. Assumption of these initial condition profiles for contaminant distribution limits the model to be suitable only for generating bounding predictions (overestimation) of peak groundwater contamination, which is consistent with the objective for these calculations.
- Both the SSL and PRG simulations applied a derived K<sub>d</sub> for Cr(VI) of 0.8 mL/g based on the results of the batch leach testing at the 100 Area. This K<sub>d</sub> value is applicable only to the residual fraction of Cr(VI) remaining in the vadose zone at present, and is not applicable to the leachable fraction that has already migrated (leached) through the vadose zone to groundwater in the past. This is a conservative value, in that this value was selected on the basis that 95 percent of the batch leach test results yielded a higher K<sub>d</sub>. As a limitation, this parameter value would not be applicable for use in a predictive model (that is to say, in a model constructed to accurately estimate future vadose zone leaching rates with minimal bias), but is rather a bounding value deliberately selected to overestimate Cr(VI) arrival in groundwater in the future from residual contamination remaining after remediation.
- The initial conditions for matric potential at the start of the flow and transport simulations represent a
  wetter vadose zone than is expected for such gravel-dominated sediments in an arid climate, thus
  allowing significantly higher water and solute flux values. This is conservative in that it results in
  more rapid movement of water through the vadose zone. This not a limitation of the model (which
  can simulate any initial matric potential), but rather is a consequence of conservative
  parameterization.
- The median hydraulic gradient value for each source area may be too low by several-fold for waste sites near the Columbia River and may be several times too high for waste sites that are far inland from the river. This a limitation of the modeling approach (but not the model itself), in which a generalized approach was adopted to calculate bounding SSL and PRG values that would be

applicable to all waste sites in a geographic area. The alternative (not adopted) would have been to model every waste site individually with geographically specific hydraulic gradient values to arrive at a SSL and a PRG value that differs for each waste site.

• The assumption of a 5 m (16 ft) thick aquifer may be non-conservative for those waste sites at locations where the aquifer thickness is less than 5 m (16 ft). As noted in Section 3.6.1, the saturated thickness of the unconfined aquifer thins towards the 100-H Area. The mapping of aquifer thickness presented in Section 3.6.1 shows, for times of year with lower river stages (for example, September) that the 5 m (16 ft) assumption is, at least seasonally, not representative. The process for developing the representative stratigraphic columns for the 100-H waste sites (Section 5.4.2) that incorporated a 5 m (16 m) aquifer included consideration of the seasonal fluctuation in aquifer thickness; however, the conservatism was placed on minimizing the vadose zone thickness by using the highest annual water table. This was, at least for some portion of the year, non-representative with respect to dilution in the saturated zone.

#### 5.9.5 Uncertainties, Assumptions, and Limitations Specific to Groundwater Modeling

Uncertainties based on the numerical equations used in modeling are expected to be small. A groundwater flow and contaminant transport model has been developed and calibrated for remedy design evaluation purposes in the 100 Area. The model development and calibration is documented in a comprehensive modeling report (*Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model* [SGW-46279] in Appendix F).

The groundwater flow model grid encompasses all 100 Area OUs. The model finite-difference grid is constructed so that the north and northeast boundaries of the flow model parallel and abut the Columbia River. The model extends southward, toward Gable Butte and Gable Mountain. The grid spacing is relatively coarse (about 100 m [328 ft]) throughout much of the domain, but it is refined (15 m [49 ft]) in the area of each 100 Area OU to support remedy evaluations.

Assumptions within the model input parameters have an effect on the simulation outcomes. The key assumptions used for 100-D/H are as follows, with other assumptions and the specific input parameters presented in *Conceptual Framework and Numerical Implementation of 100 Areas Groundwater Flow and Transport Model* (SGW-46279) in Appendix F.

Predictive simulations were based on transient-state (that is, time-varying) conditions in the aquifer that reflect water level changes because of river stage variation. The modeling period corresponds to a 77-year period (CY 2011 to 2087). For the period 2011 to 2037, the modeling period consists of a series of 12 monthly stress periods that are repeated in the same sequence. The stress periods correspond to monthly average river stages, each representing the average river stage for the particular calendar month over the period 2006 to 2010 (excluding 2007 values, when the river stage variation pattern was inconsistent with the other years). It is assumed that these conditions are representative of the typical conditions in the field and that future conditions will not vary significantly.

Groundwater flow is simulated as 3D using four layers to represent the Hanford formation (always present in Layer 1) and the Ringold Formation unit E (typically represented by Layers 2 through 4). The base of the model is assumed to be the top of the RUM where present and the top of the basalt where the RUM is absent. Underlying 100-D, the water table mainly occurs within the Ringold Formation unit E. Across the Horn area, east and northeast of 100-D, the water table occurs primarily within the Hanford formation. The water-bearing units within the RUM are not included in this representation; as noted earlier, Cr(VI) contamination occurs in the first water-bearing unit of the RUM but is limited in areal extent beneath 100-H and at one location in the Horn, near 100-D. Further east into the Horn area,

no Cr(VI) contamination is observed in this unit. Thus, the uncertainty introduced to the model from omitting this feature is considered low.

In Evaluation of Potential Hydraulic Capture and Plume Recovery from the Ringold Upper Mud (RUM) in the 100-HR-3 Operable Unit (OU) (ECF-100HR3-12-0025; Appendix F), screening-level calculations are performed in support of the 100-HR-3 RI/FS to evaluate time-dependent zones-of-contribution and contaminant recovery under various pumping scenarios from wells screened in the upper portion on the RUM. These simulations consider the various potential aquifer configurations of the first water bearing unit within the RUM, namely whether it is confined, semi-confined, or leaky, as well as its potential to be connected to the Columbia River. A secondary source within the RUM material, separating the unconfined and lower aquifers, is not present, as demonstrated by analytical sample results from that zone (Section 4.3.19 and 4.3.21). The calculation demonstrates that pumping from the RUM unit should be an effective remedial strategy, as discussed in Chapter 9. Additional evaluation of groundwater contamination removal during pumping activities from the first water bearing unit of the RUM has been conducted.

The principal aquifer property specified in the flow model is the spatially varying hydraulic conductivity of the saturated aquifer materials. Estimates of hydraulic conductivity compiled as part of the model data package were tabulated and assigned to their corresponding aquifer unit. Following are the mean values for the aquifer hydraulic conductivity that resulted from the model calibration process:

- 19 m/day (62 ft/day) for the Ringold Formation unit E
- 63 m/day(206 ft/day) for the Hanford formation

Areal recharge from precipitation was specified based on information included in *Groundwater Data Package for Hanford Assessments* (PNNL-14753). An electronic version of the recharge package developed in this report was obtained, and the data were spatially distributed to the model grid cells and were subsequently adjusted during model calibration. Based on the results of the model calibration, the recharge value was set equal to 12 mm/yr throughout much of the model domain. This value is a spatially based average of distributed recharge rates applied over a large area with variable surface soil types and vegetation cover types for present day conditions represented by the groundwater model. As such, this rate is not directly comparable to, but is consistent with, recharge rates applied for vadose zone models of individual waste sites.

Initial values for effective porosity and specific yield for the entire aquifer to use in the inverse model calibration process were identified by review of published previous models for the Hanford Site. The calibrated values obtained from the inverse model calibration process were 18 and 10 percent, respectively, which are in the range of values documented in previous investigations for the Hanford Site.

The initial distribution of each COC in groundwater within the 100-HR-3 OU was obtained using maximum sampled COC concentrations at each monitoring location during the period 2009 to 2010. For the purposes of predictive modeling, is assumed that no continuous source is present in the aquifer or vadose zone that would affect the contaminant distribution. At present, there are known vadose zone waste sites that represent potential sources of Cr(VI) contamination (e.g., see Section 4.3.20). However, these sites are currently under active remediation to remove contamination sources, and thus are not included in predictive modeling for the future condition.

# 5.10 Summary of Contaminant Fate and Transport

Intentional and unintentional releases of primary waste source materials occurred during nuclear material production at the Hanford Site. The EPCs of each remediated waste site, soil group, and COPC, as well as

the results of vadose zone soil analysis for soil samples collected during the previous CVP, LFI, and this RI, were compared to the SSLs calculated using the irrigation recharge scenario with 100:0 and 70:30 profiles as well as the PRGs calculated using the nominal scenario (that is, non-irrigated, natural recharge conditions) with 100:0 and 70:30 profiles. After excluding COPCs with peak concentration times greater than 1,000 years, no waste sites were found to exhibit EPCs greater than the SSLs for residual contamination in the vadose zone. None of the EPC concentrations for metals fell outside the reported background concentration range for Hanford Site soils. Metals are believed to be representative of naturally occurring background concentrations, with potential contribution from historical agricultural application of lead arsenate pesticides to orchards that pre-dated Hanford Site operations near 100-H. Waste sites that have not yet been remediated were carried into the FS for evaluation with COPCs based on process knowledge.

Groundwater contaminant flow and transport modeling over an extended future period and historical monitoring indicate that the groundwater pump-and-treat systems have provided, and will continue to provide, protection to the Columbia River along the shoreline in almost all areas by achieving the state water quality standard (WAC 173-201A, "Water Quality Standards for Surface Waters of the State of Washington") (10 µg/L) for Cr(VI).

The source area waste sites that have been remediated under interim action did not exceed the SSLs or PRGs protective of groundwater and surface water for Cr(VI). While the RI data indicate that contamination in the vadose zone has been remediated, groundwater monitoring indicates that there is potential for low level residual contamination. Unremediated waste sites have significant inventory in the shallow vadose zone. At some locations (for example, the 100-D-100 and the 100-D-104 waste sites), RTD down to the water table may be required to completely remediate the contaminated soil.

In 100-H, pumping is currently being conducted within the first water-bearing unit of the RUM. Characterization of the RUM confirmed that Cr(VI) contamination consistent with cooling water is present in this horizon below the unconfined aquifer only in localized portions of 100-H. The cross sections presented in Chapter 3 indicate that a significant thickness of silt occurs between the contaminated RUM water-bearing unit beneath 100-H and the channel of the river, blocking the pathway further out from the shoreline. Therefore, continued pumping of this water-bearing unit will capture the Cr(VI) and protect the river farther out into the channel from the shoreline by achieving the state water quality standard (WAC 173-201A, "Water Quality Standards for Surface Waters of the State of Washington").

Plume migration patterns, as estimated by the model, indicate a diminishing footprint of the Cr(VI) plume because of pump-and-treat operations. Concentrations in groundwater above 20  $\mu$ g/L appear sufficiently controlled by the current combined extraction/injection activity across the area of interest as shown by the hydraulic containment in 2012 evaluation (Section 5.8.3.1). Model results indicate that concentrations between 10 and 20  $\mu$ g/L are fairly well contained, except in areas west of 100-D and east of 100-H where the plume slowly discharges to the river. Based on the modeling results, Cr(VI) concentrations in groundwater underlying 100-D/H will decline over time, although the rate of decline is not uniform across the area of interest.

Strontium-90 concentrations in groundwater above the MCL are within the capture zone of the recovery wells at 100-D, but small areas are outside the capture zone at 100-H. Recirculated strontium-90 concentrations reinjected into the aquifer are always below the MCL and modeling results suggest that concentrations will decline over time.

Nitrate concentrations in groundwater above the MCL are within the capture zone of the recovery wells although a small area is outside the capture zone in 100-D south. Recirculated nitrate concentrations

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injected back into the aquifer are always below the MCL and modeling results suggest that concentrations will decline slowly over time.

Simulation of the base case groundwater contaminant plume migration indicates that there is a clear basis for remedial action to address the existing plumes underlying 100-D/H. Turning off the pump-and-treat systems at the end of 2012 (as represented in the base case groundwater modeling) will result in the existing plumes persisting and slowly discharging into the Columbia River. Without the implementation of remedial action, such as the current pump-and-treat systems, unacceptably large concentrations of groundwater contaminants (for example, Cr[VI]) will continue to discharge to the Columbia River.

The evaluation of EPCs indicated that remediated waste sites should not contribute to continuing groundwater contamination based on lack of any exceedances of SSLs protective of groundwater or surface water (Section 5.7.3). Uncertainties remain regarding the potential for continued contribution of residual vadose zone contaminants to underlying groundwater. Strategies for addressing potential residual contamination will be discussed in the FS. Remedial alternatives evaluated in the FS portion of this report will consider monitoring requirements that will verify the assumptions for vadose zone contaminant behavior. Existing groundwater plumes of Cr(VI), strontium-90, and nitrate near the reactor condensate cribs, the FSBs, the retention basins, the cribs, and the cooling water head houses should be considered for specific monitoring of potential future vadose zone contributions.

Chapter 5 describes and predicts how quickly or slowly contaminants migrate, and their potential to subsequently enter the Columbia River (however, note that these predictions are limited to an effective rate of arrival; it is not an objective or function of this model to predict specific locations of upwelling in the riverbed). The potential to be harmful depends on specific human and environmental receptors, as well as exposure times and patterns that might bring receptors and contaminates into contact. The ways that the contaminants could come into contact with, and affect, human health and the environment are called pathways. Chapter 6 addresses the human health pathway; scenarios of how humans might come into contact with contaminants in the setting with resultant health effects are evaluated. Chapter 7 addresses the biological receptor pathway. Scenarios of how plant, animal, bird, or invertebrate species might come into contact with contaminants in the setting and be affected are evaluated in Chapter 7.

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